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W. A. Van Winkle

A Study of the Determination of the
Halogen in volatile Organic Com-
pounds

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A STUDY OF THE DETERMINATION OF THE HALOGENS
IN VOLATILE ORGANIC COMPOUNDS

BY

WILLIAM ALEXANDER VAN WINKLE

B. S. University of Michigan, 1911

M. S. University of Illinois, 1917

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

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IN CHEMISTRY

IN

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THE GRADUATE SCHOOL

August 4 1919

Mr. VanWinkle uses data as singular several times, as p.

page 35 middle paragraph sixth word should be "bringing" not "hinging".

" 43 4th line, "furance" should be "furnace"

Recommendation concurred in"

Geo. D. Beal
Roger Adams
J. H. Reedy
Morgan Brooks

Committee
on
Final Examination*

*Required for doctor's degree but not for master's

46.3.23

1920
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UNIVERSITY OF ILLINOIS

THE GRADUATE SCHOOL

August 4 1919

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
SUPERVISION BY WILLIAM ALEXANDER VAN WINKLE
ENTITLED A STUDY OF THE DETERMINATION OF THE HALOGENS
IN VOLATILE ORGANIC COMPOUNDS
BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

G. M. P. Smith.

In Charge of Thesis

J. H. Farr

Acting Head of Department

Recommendation concurred in*

Geo. D. Beal
Roger Adams
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Kinnicutt and Sweetser² showed that the method, recommended by Schulze³ in which this was the basis for analyzing compounds with halogen in the side chain, would not work in the case of such compounds as phenyl dibromopropionic ethyl ester, and B-monobromocinnamic acid.

As a rule, the iodine compounds are the most reactive, followed in turn by those containing bromine and chlorine.

The above methods are not only limited to special classes of organic halogen compounds, but also do not lend themselves well to volatile substances.

Dry Treatment:

This is best represented by the Liebig or Lime method, which consists in heating the substance in the presence of calcium oxide, thus decomposing it. The method is general in its application, even to volatile substances, although more care must be exercised in the latter case. While the values for chlorine and bromine are usually satisfactory, those for iodine may not be so.⁴ The large quantity of calcium nitrate formed in the subsequent procedure may lead to low halogen results, due to the solubility of the silver halides in concentrated calcium nitrate.⁵ Trouble is sometimes encountered because of a turbid solution caused by the suspended carbon formed during the decomposition.

The method of Pira and Schiff⁶ is only a modification of Liebig's; the decomposition of the substance being carried out in a special arrangement of crucibles with a mixture of sodium carbonate and calcium oxide. It has the advantage of the use of platinum or



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nickel crucibles in place of a glass combustion tube, but is far less applicable to volatile compounds.

Splitting Out:

This method depends upon the special reaction in which an active halogen is split off in conjunction with hydrogen, by the use of alcoholic potash or an alcoholic solution of potassium ethoxide resulting in the formation of an ioniable halogen compound. It is rather limited in its application, not only because of the chemical nature of the compounds, but also since a volatile substance might escape during the reaction.

Reduction:

This depends upon the action of nascent hydrogen upon compounds containing halogen, the latter being replaced by and removed in combination with hydrogen; the halide then being in a condition for determination by the usual methods of inorganic analysis.

Kekulé used sodium amalgam and water to remove the halogen in substituted acids.⁷

More recently the nascent hydrogen has been generated by the action of metallic sodium or potassium upon alcohol, the organic halogen compound having previously been dissolved in the latter.

The method, first suggested by Stepanow⁸, who obtained some excellent results with such compounds as chlorobenzene, hexachlorobenzene, p-chlortoluene and α -bromonaphthalene, has been both recommended and condemned. Bacon⁹ attempted to apply it to some refractory aromatic acids, containing halogen, but the results were entirely unsatisfactory. Investigation led him to believe that

rather strict attention should be paid to the relation between the quantity of substance used, the nature of the halogen, and the quantity of alcohol and metallic sodium used; also to the duration of the addition of the latter. He then obtained satisfactory values.

Maryott,¹⁰ too, was unable to obtain good results with chlorobenzene. He reported that before enough sodium had been added to effect complete reduction, the liquid became pasty, owing to the separation of sodium ethylate, and this localized and greatly hindered the action of the sodium". He substituted potassium for sodium and was able to obtain satisfactory values, not only upon the above compound, but also upon two with which Bacon has failed to get good results.

Walker and McRae¹¹ state that they were unable to obtain satisfactory values when they used the modification of Stepannow's method, proposed by Bacon. They used monobrombenzene and α -bromonaphthalene. "Forty trials were made" upon the former compound, "all results being low, and in no case were duplicates obtained which agreed, which showed that the reduction was incomplete and irregular". In summary, they add, "We are forced to conclude, therefore, that the method is not of general applicability and especially cannot be used with difficultly reducible substances".

Drogin and Rosanoff¹² also found that they could not obtain good values by following Bacon's directions. After much experimentation they report "increasing Bacon's amount of sodium by 10% and at a later stage carrying out the Volhard halogen determination

with all necessary care, led to uniformly excellent results in all cases without exception". This is substantiated by the results obtained from sixty-four consecutive analyses of eleven substances belonging to different classes. One point they strongly emphasize is that "ordinary absolute alcohol should be redistilled from metallic sodium, about 10 grams of sodium being used per liter of alcohol". They also found that a certain definite relation must be maintained between the quantity of sample, including the nature of the halogen present, the alcohol and the metallic sodium.

While the method has apparently been developed to a satisfactory stage, the question arises whether the conditions of operation are not too exacting for general use. Further, of the ~~the~~ eleven compounds chosen for experimentation, none are really volatile substances, the two with the lowest boiling points being chlorobenzene and brombenzene, at 132° and 156° C, respectively. Of course, they were attempting to show that the kind of compounds thought not to be attackable by this treatment, will yield to it with satisfactory results.

Oxidation:-

Not By Combustion:

Wet treatment--

This has usually consisted in digesting the substance with such reagents as nitric acid, potassium dichromate, potassium persulphate and potassium permanganate, usually in a sealed tube, in the case of the first reagent (Carius Method) or in a crucible or beaker in the case of the others.

The Carius method yields very satisfactory values, but it has some disadvantages which are too well known for the writer to discuss them.

In regard to the various other schemes involving wet oxidation, which have been proposed from time to time, they have no special advantage over previous methods, are rather limited in the nature of the compounds to which they may be applied, or do not lend themselves very well to rather volatile substances.

By Fusion:

In brief this consists in fusing the halogen compound with such oxidating agents as sodium nitrate, potassium nitrate and sodium peroxide, often mixed with sodium carbonate or potassium carbonate.

¹³
Berzelius used a mixture of sodium carbonate and ammonium nitrate, carrying out the fusion in a porcelain crucible.

¹⁴
Volhard used a mixture of potassium nitrate and sodium carbonate and fused in a porcelain crucible.

¹⁵
Pringsheim suggested the use of sodium peroxide, carrying out the fusion in his well-known bomb.

¹⁶
Parr applied the sodium peroxide fusion in a specially constructed bomb from which none of the products could escape during the oxidation. Only the analysis of one substance, aniline chloride, was given, for which a value of 27.63% chlorine was found, against the theoretical of 27.36%.

¹⁷
Lemp and Broderson followed up this work in an investigation in which they used the Parr Sulphur Bomb, and the reagents, sodium peroxide and potassium nitrate, to which either a few tenths of a

gram of either benzoic acid or sugar were added to aid in the fusion. A sample of from 0.20 to 0.25 grams was used. Volatile liquids were sealed and weighed in a small bulb which was broken within the closed bomb, in the presence of the fusion reagent.

The fusion was effected by heating the lower portion of the bomb to a red heat and then cooling in running water. The contents were removed, dissolved in water and boiled to remove the excess of peroxide. Next an excess of standard silver nitrate was added, then acidified with ^{nitric} acid and hydrazine sulphate added to insure removal of all oxy-compounds. Finally the excess silver nitrate was titrated without filtering, with standard thiocyanate solution.

While, in general, the values given are fairly good, yet they were not checked by some other method of analysis. The discrepancies are attributed to poor fusions, impure reagents and impure organic compounds.

Analyses on twelve chlorine, six bromine and one iodine compounds (all rather stable) are given, but only one liquid, p-chlorotoluene (B.P. = 162.3° C), was used, which is hardly enough to warrant the belief that the method could be successfully applied to rather volatile compounds.

Combustion:

This method of analysis, with some modifications, has been proposed from time to time. In principle, nothing could be more simple. The difficulty has been largely in the manner in which the combustion has been carried out, and in the method used for deter-

mining the halogen in the products of combustion and decomposition. Most of the methods are open to the general objection that one is obliged to pack a combustion tube with special reagents, which, in some cases, are likely to fuse upon the combustion tube and so are not so easily removed. Also the tube (glass) does not last for many determinations. Often attention must be given during the entire combustion.

Warren¹⁸ burns the substance in a combustion tube in a stream of oxygen and absorbs the halogen with various oxides, such as zinc oxide, lead dioxide and cupric oxide, placed within and towards the end of the tube. The oxide, with absorbed halogen, is then treated with a solution of sodium carbonate, to extract the halogen and then the latter is determined in the usual manner. Only chlorine compounds were used, with results varying from the theoretical as much as 4.5%.

Brugelman¹⁹ also burns in a stream of oxygen, but uses calcium oxide to absorb the halogen. Good values were obtained upon substances used including a few volatile substances. Determinations were not made in duplicate nor checked by another method.

Dennstedt²⁰ burns in oxygen, using platinum black as a catalytic agent, and absorbs the halogen, in the case of chlorine and bromine compounds, with lead dioxide; in the case of iodine with metallic silver; the absorbing reagent being in and toward the end of the combustion tube. The method for the subsequent procedure, when lead peroxide is used, is similar to that of Warren; when metallic silver, the increase in weight is considered due to iodine. Only the

results on one substance, p-bromophenylsulphourea, $\text{CS}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Br})_2$, are given, which check within 0.21 plus percent of the theoretical. The work was not checked by another method of analysis.

Plimpton and Graves²¹ introduce the volatile organic halogen substance in "the state of vapor into the flame of a bunsen burner when the halogens are obtained chiefly in combination with hydrogen, and in small quantity in the free state. The products of combustion are then drawn through suitable absorbers, containing sodium hydroxide, and the halogens so collected are then estimated in the usual way". A special apparatus is devised for this method of analysis. Apparently, from what is said, it is not easy to control the combustion, and it must be given constant attention. Sulphurous acid is used to reduce the oxy-compounds which may have been formed, before adding any excess of silver nitrate, which is determined in the usual manner. Good values were obtained upon ethyl bromide and iodide; carbon tetrachloride; ethylene chloride; bromide and chloriodide; amyl chloride; and acetylene bromiodide; also upon benzal chloride. Only in the latter instance was some other method used for checking. In the case of the double halides, the value given is the percentage sum of the two halogens present, neither of the individual values being given.

Zulkowsky and Lepéz²² burn the halogen compound in a glass combustion tube in a stream of oxygen using platinized quartz as a catalytic agent and absorb the product, in the case of chlorine compounds, in an ammoniacal solution of hydrogen peroxide; while, with bromine and iodine, in a solution of potassium iodide. They believed that in the case of chlorine compounds, the halogen

existed in the decomposition product as hydrogen chloride, while in bromine and iodine, in the free state. They did not use sodium or potassium hydroxide since they thought the accuracy would not be so great. They also point out that the fog which appears in the absorption train, when using ammonia, is an indication that decomposition products are still leaving the combustion tube.

They find that unless proper regard is paid to the excess of hydrogen peroxide used, oxy-compounds may be formed.

Their absorption train consists of an Erlenmeyer flask, a Peligot U-tube and a small vertical tube which is packed with glass wool soaked with reagent; reagent also being placed in the other two parts of the train. The Peligot U-tube is not used in the case of bromides and iodides.

The absorption solution, after removal of excess hydrogen peroxide, is analyzed for chlorine in the usual manner; in the case of bromine and iodine, the determination is iodometrically.

They found considerable difficulty in the case of chlorine compounds, since the platinum was found to retain rather tenaciously some of the chlorine, which could be removed only with excessive heating.

A glass combustion tube was used, with the exit end drawn out and bent downward so that it would pass through the two-hole stopper of the Erlenmeyer flask and dip into the absorption solution.

Non-volatile solids are weighed in a porcelain boat; while solids, slightly volatile, are weighed in a small glass tube, sealed at one end. Liquids are weighed in a special drawn out, pipette

shaped tube, sealed at one end. In all these three cases, the container, with sample, is placed within and near the entrance end of the combustion tube. By special attention in the application of heat, the sample is volatilized.

In the case of volatile liquids, a tube, with a bulb blown in the middle, serves as the container. After the sample is introduced into the latter, both ends are sealed off. One end of the container is then shoved thru a two-hole stopper (the other hole is for the tube thru which the oxygen enters) in the entrance end of the combustion tube and by a turning of the oxygen tube, the end of the sample holder within the combustion tube is broken. The other end is now broken and connected to the source of oxygen, enough being allowed to pass, so that with the warming of the bulb of the container, the passing oxygen carries the sample into the combustion tube where it meets the excess oxygen. The device for volatile liquids is somewhat clumsy.

In the majority of the analyses, they obtained good values, which check well with those obtained by the Carius method.

²⁴
Klason suggested burning the substance in a stream of air or oxygen mixed with nitrous fumes, the latter being introduced just ahead of the sample, which is in about the middle of the combustion tube, the burning taking place in the presence of platinum foil.

In the case of bromine and chlorine the products are passed into a solution of silver nitrate; while with iodine compounds only into water, the iodine later being taken into solution with sulphurous acid or alkali sulphite, then neutralized and the iodine precip-

itated with silver nitrate. No analytical data is given and so one has nothing upon which to base judgment upon.

Reid²⁵ suggests a method in which the sample is burned in a very slight excess of oxygen and the products absorbed by a mixture of metallic silver and silver oxide, the latter being in a small silver boat placed toward the exit end of the combustion tube, which must be held at a temperature of about 270° C. The combustion takes place in the central part of a transparent combustion tube, which at that point is strongly heated. The rate of combustion is regulated by careful heating, with a free flame, that part of the combustion tube containing the boat with sample.

In the case of volatile substances (liquids) the sample is weighed and sealed within a small bulb and the latter broken within a specially designed U-tube, after the latter has been connected to the combustion tube. This permits the sample to be carried into the latter in the vaporized state by the incoming oxygen.

Having the weight of the silver boat, boat plus metallic silver, boat plus metallic silver and silver oxide, one is then directed as follows: "To find the weight of the halogen absorbed, deduct from the weight of the boat containing the oxide, the amount that this oxide would lose on reduction and subtract this corrected weight from the final weight of the boat". After the combustion is over, and the tube has cooled to 170° C., he reduced any silver oxide in the silver boat by passing in hydrogen. Metallic silver is used to absorb the free halogen, and the oxide of silver to take up the halide, which, it was recognized, always exists to some

degree, in the combustion of chlorine, bromine and iodine compounds.

Eleven analyses are given; three upon p-bromobenzoic acid; four upon p-chlorobenzoic acid; and four upon ethyl iodide; all of which check well with the theoretical. No analyses by another method are given.

From the above survey of some of the more important methods which have been offered for the determinations of the halogens in organic substances, particularly in the case of volatile compounds, it appears that there is still plenty of room for improvement. The writer feels that a combustion method, which involves simple, yet efficient and easily controlled apparatus, which demands only simple reagents, no catalytic agents, only air for combustion, and one in which little weighing is involved, will prove welcome. The experiment described in the Introduction suggests that such a method can be worked out.

III

E X P E R I M E N T A L

Choice Of Standard Substance:-

It was felt that the material should be rather volatile; obtainable in a high degree of purity, and fairly stable; have a high halogen content, in order to show up any errors in the method or analytical work; contain only one halogen; and should contain chlorine, rather than bromine or iodine, since the former is so much more volatile. Several compounds might have been chosen; chloroform was taken since it has these characteristics and was available.

While the material used was fractionated and the portion boiling between 60-61° C. was taken for analysis, the main idea at this stage was to ascertain whether consistent results were obtainable, regardless of whether they were 100% of the theory; perfection of apparatus would follow.

Determination Of Halogen:-

Reagents:

The following reagents were used in this investigation:

Sodium hydroxide, approximately 5 N, which, for the first 30 determinations, was made from metallic sodium in order to avoid a correction for halogens in the reagent in the titration by the Volhard method; from No. 31 on, the stick sodium hydroxide was used.

Sodium sulphite, approximately 3 N, which, for the first 30 determinations, was made from the sodium hydroxide from metallic

sodium, and purified sulphur dioxide. But from No. 31 on, the stock sodium sulphite was used.

Dilute sulfuric acid, 1 : 3 of water.

Dilute nitric acid, 1 : 3 water.

A saturated solution of potassium permanganate.

Standard silver nitrate solutions, both 0.1 and 0.2 N.

Standard ammonium and potassium thiocyanate solutions, both 0.05 and 0.10 N.

Ferric alum indicator, a saturated solution of ferric alum to which concentrated nitric acid was added until the lightening of the deep brown color ceased.

Purified sodium chloride for standardization of AgNO_3 solutions. It was precipitated from a saturated solution by gaseous HCl and washed with concentrated, C. P., hydrochloric acid, then centrifuged, and finally heated several hours at about 700°C .

Purified potassium bromide and iodide for standardization. In each case the material was recrystallized twice, then centrifuged, and finally heated several hours just below the melting point.

Pure potassium chlorate for standardization.

Absorption and Reduction:

Several basic solutions suggested themselves, but due to cheapness, availability and probable efficiency and the fact that sodium halides are not carried along in air currents as ammonium salts are, a solution of approximately five normal sodium hydroxide was used, always of such volume as to have present at least five or more times the theoretical amount.

It was realized that during the decomposition and combustion, particularly at elevated temperatures, more or less free halogen would be produced, even if hydrogen were present in the compound, and that absorption in an alkaline solution--especially if it became warm--would result in the formation of oxy-compounds, which would have to be reduced to the halide state before a Volhard analysis was attempted.

After experimenting with hydrogen peroxide, metallic zinc and sodium sulphite as reducing agents, in which experimental work a known weight of pure potassium chlorate was used as a standard, there did not seem to be any question about the efficiency of the sodium sulphite, since, using it, the chlorine values found were practically theoretical, while in the case of hydrogen peroxide and metallic zinc, values averaging approximately about 8.5% and 81% of theory, respectively, were obtained. And what is more to the point, the presence of an excess of sulphite during the actual moment of absorption, would prevent completely the formation of any oxy-compounds.

Removal of Excess Reducing Agent:

This of course would be necessary before a Volhard determination was attempted. On acidifying with dilute sulphuric acid, sulphurous acid would be liberated. During some of the earlier determinations, up thru No. 50, the sulphur dioxide was boiled out. But the time involved was too long and so from then on the method of removal consisted of oxidation with a strong solution of potassium permanganate, added carefully until a faint pink appeared, which was immediately discharged by a small drop of the sodium sulphite

solution.

That both methods are satisfactory, even in the case of bromine and iodine, is shown by the data given in Tables I and II, with their accompanying notes.

TABLE I

Showing efficiency of methods for
removal of excess sulphite

Using Pure NaCl as a Standard			
Acidifying with dil. H ₂ SO ₄ and boiling		Acidifying with dil. H ₂ SO ₄ and titrating with KMnO ₄	
Sample (grams)	% Cl found	Sample ¹ (grams)	% Cl found
0.3409	60.47	0.7217	60.60
0.4042	60.62	0.7222	60.58
0.3570	60.66	0.7313	60.71
0.3688	60.62	0.7276	60.65
0.3513	60.61	0.5075	60.42
0.3500	60.45		
1.5073	60.61		
1.5001	60.55		

Notes applying to table I:

Theory = 60.65% chlorine

The following was obtained gravimetrically, using Gooch crucibles:

Sample ² (grams)	% chlorine found
2.0000	60.63
2.0000	60.65

² The samples were made up to 250 cc. and
50 cc. portions taken for analysis

Samples weighing 1.5073 grams and 1.5001 were also made up to 250 cc. and 50 cc. portions taken for analysis; no aliquot was taken of the other samples in this column.

In all cases in column (1), the samples were made up to 250 cc. and 100 cc. portions taken for analysis.

TABLE II

Showing efficiency of methods for
removal of excess sulphite

Using Pure KBr as a Standard

Sample ¹ (grams)	No absorption reagents added	Method	
		Boiling out	Using KMnO ₄
		Percent of Br found	
3.5722	67.55	67.58	67.71
3.5688	67.54	67.59	67.68

Using Pure KI as a Standard

	Percent iodine found		
4.9823	76.51	76.66	76.69
4.9799	76.55	lost	76.63

Notes applying to Table II:

Theory = 67.16% Br; and 76.46% I.

Analytical values may be slightly high due to the possible presence of chloride in both bromide and iodide.

Samples (1) were made up to 250 cc. and 50 cc. portions taken for analysis.

No gravimetric analyses were made in the case of the bromide and iodide.

Titration:

The absorption solution, containing the halogen as halide, was treated with 25 cc. of dilute H_2SO_4 , the excess SO_2 removed, up to determination No. 51, by boiling out, after that with KMnO_4 solution, and then standard AgNO_3 solution was added until an excess of about 5 cc. was present. Then a few cc. of dilute HNO_3 were added. Usually on shaking the Erlenmeyer flask for a minute or so the precipitate coagulated immediately; if not, the flask and contents were warmed on the steam bath.

In all cases the precipitate was filtered out, even in determinations for bromine and iodine, since in the latter cases, the NaOH and Na_2SO_3 then being used contained chlorine.

The solutions were filtered in the cold, using suction, and washed with 1% HNO_3 until no turbidity was obtained on addition of HCl to the filtrate.

Then 5 cc. of ferric alum indicator was added, followed by enough dilute HNO_3 to lighten the color a little and then the excess AgNO_3 was titrated with standard potassium or ammonium thiocyanate solution, with normalities half the silver nitrate solution which had been used.

Titration Table:

All titrations were made in artificial light. For this purpose a special titration table was designed and partially constructed by the writer (See Plate I).

The base, made of one inch board, 26-1/2" x 11", has inlaid upon its upper surface and placed flush with the border, a glass

Plate No.1.

Scale, $\frac{3}{16}'' = 1''$

Titration Table

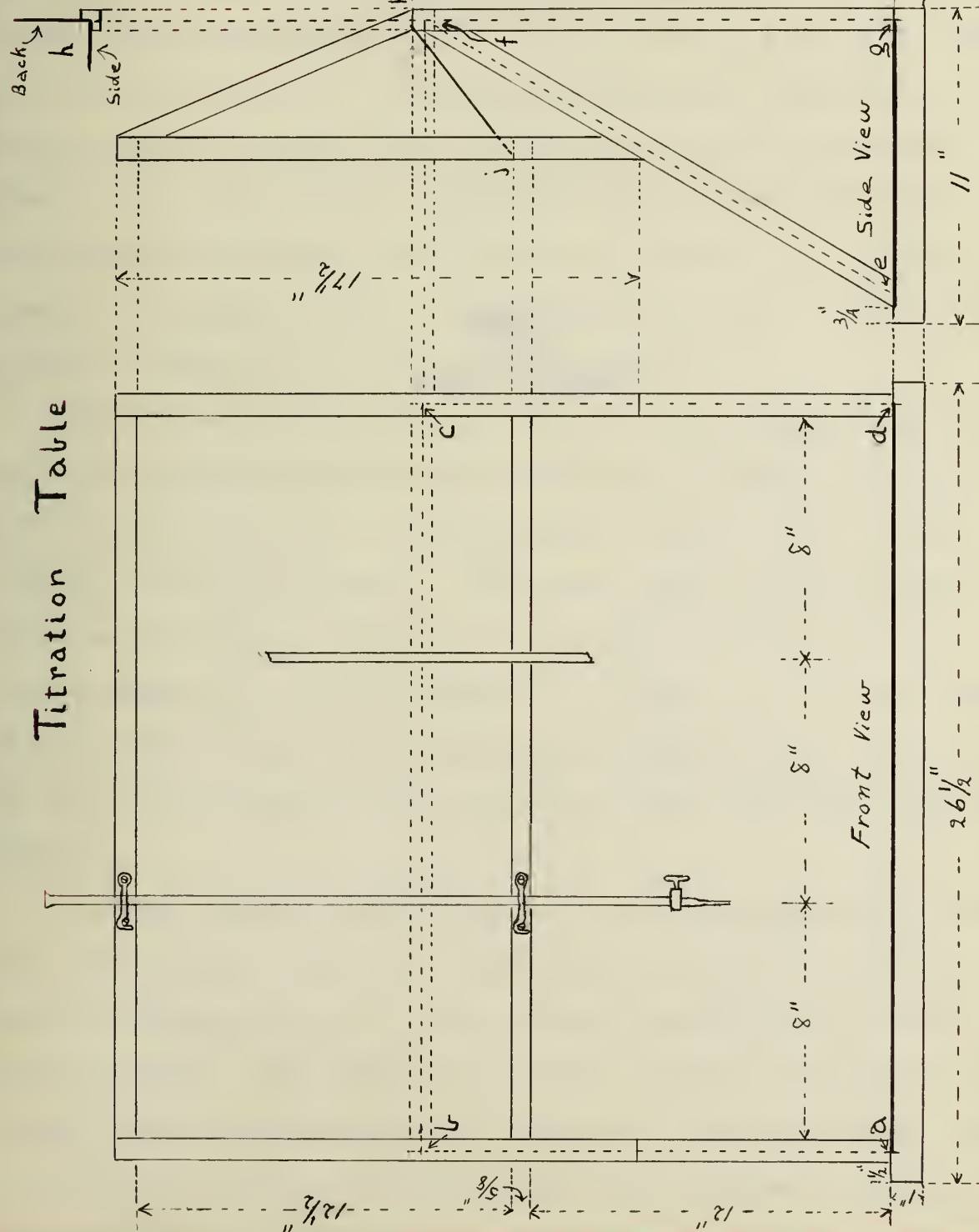


Fig. 1

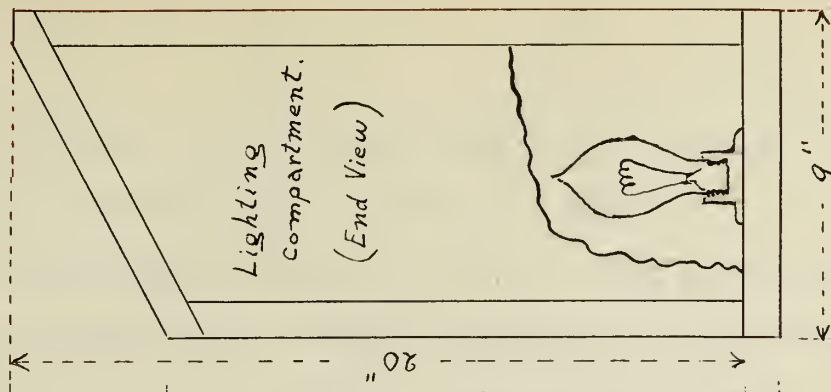


Fig. 3.

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plate 25" x 10", the under side of which has three coats of white (lithopone) paint. See heavy line in Figs. 1 and 2.

Mounted upon this base, as shown in Figs. 1 and 2, is a hard wood frame, made of strips $5/8"$ x $5/8"$, for supporting the two burettes and also the two ground glass triangular ends and the ground glass rectangular back. See e, f and g in Fig. 2; and a, b, c and d in Fig. 1. The glass plates form a triangular prism, lying upon its smallest side and with its largest side missing and open toward the operator. Although little direct light would hit the eyes of the worker, as he stands in position in titrating, a special rectangular screen of ground glass $23-1/2"$ x $5-1/2"$ is placed as shown by the end, j-k, in Fig. 2.

Each burette is held in position by two, spring-brass, hooks, which turn and hook upon screws which can be adjusted so as to hold the burette firmly, yet loosely enough to permit easy raising or lowering during titration. The wooden frame, where it touches the burettes is slightly grooved. To allow insertion for about $1/8"$ of the edges of the glass plates, the frame is slotted or sawed where needed. This insures the plates being held in a firm position. In Fig. 2, h indicates how the end and back plates are butted together.

Placed directly back of and set up snugly against the rear of the table (when in use) is a lighting compartment, an end view of which is shown in Fig. 3. It covers the entire rear of the titration table. Two 100-watt, nitrogen filled, blue glass (or daylight) lamps are used, each one being in a position (front view) in line with a burette. Only the view from the side is shown in Fig.

3, by the cut-away side. A convenient switch (not shown in drawing) turns the lamps on and off.

The base of the lighting compartment is of 7/8" board and its upper surface is covered with asbestos board of such thickness that its upper surface is on a plane with that of the base of the titration table. This is to avoid shadows. The ends, back and sloping top, with the exception of the supporting wooden frame consist of asbestos board. The latter insures a more uniform diffusion of light, due to its roughened, dull white surface.

All wooden parts are, of course, painted white.

An electric lamp (not shown) placed on top of the lighting compartment and on a line, front view, mid-way between the burettes, facilitates the reading of the latter.

The ground glass plates are ground only upon one side and the smooth surface is toward the burettes. This makes it easier to clean the plates in case any solution is spattered on their surfaces.

Analysis With Electric Furnace:-

Sample Holder:

This first took the form of a small, glass capped, U-tube, in which the sample was weighed and from which it was drawn thru the combustion tube, etc., by means of gentle suction. After experimenting with that style and numerous other designs of holders, in which the sample was weighed and volatilized by aspiration, the conclusion was drawn that the only type of apparatus which would be 100% efficient, one from which none of the sample weighed out could escape into the air, especially before the connection to the com-

bustion tube was made, would be one that permitted the breaking of a small glass bulb, containing the weighed sample, after all else was in readiness. It must also be one in which back diffusion is not possible and one which permits proper control of excess air. Also, since many organic compounds attack and are absorbed by common cork and rubber stoppers, either they must be eliminated or else a barrier of some sort introduced.

The holder which was finally adopted in the preliminary work is shown in Fig. 2; A, being a side view; B, a rear view; D, the size and kind of a glass bulb used, in which the sample was sealed and weighed; and C is the ground glass stopper and plunger, which, on putting in place, breaks the bulb and seals up the apparatus.

Connection to the combustion tube is by means of the capillary (1 mm.) arm S, which is made gas tight by means of a small bushing made of gum rubber tubing.

The air comes in thru the capillary (1 mm.) tube, d, and enters the holder proper at O, thus keeping the volatile sample away from that end of the apparatus.

By rotating, with the arm, S, as an axis, the sample (a liquid) can be caused to run to the place, a, in which position the incoming air sweeps over it; or up into the part, b, which then permits the bubbling of the air up thru the liquid sample. Of course, resort is also to be had to either cooling or warming the holder. This style of holder was used in the following determinations: Nos. 55-80, 91-104 and 105-108.

It was found that moistening the ground glass stopper just before inserting resulted in a perfect air tight seal, the moisture

Fig. 2.

Holder

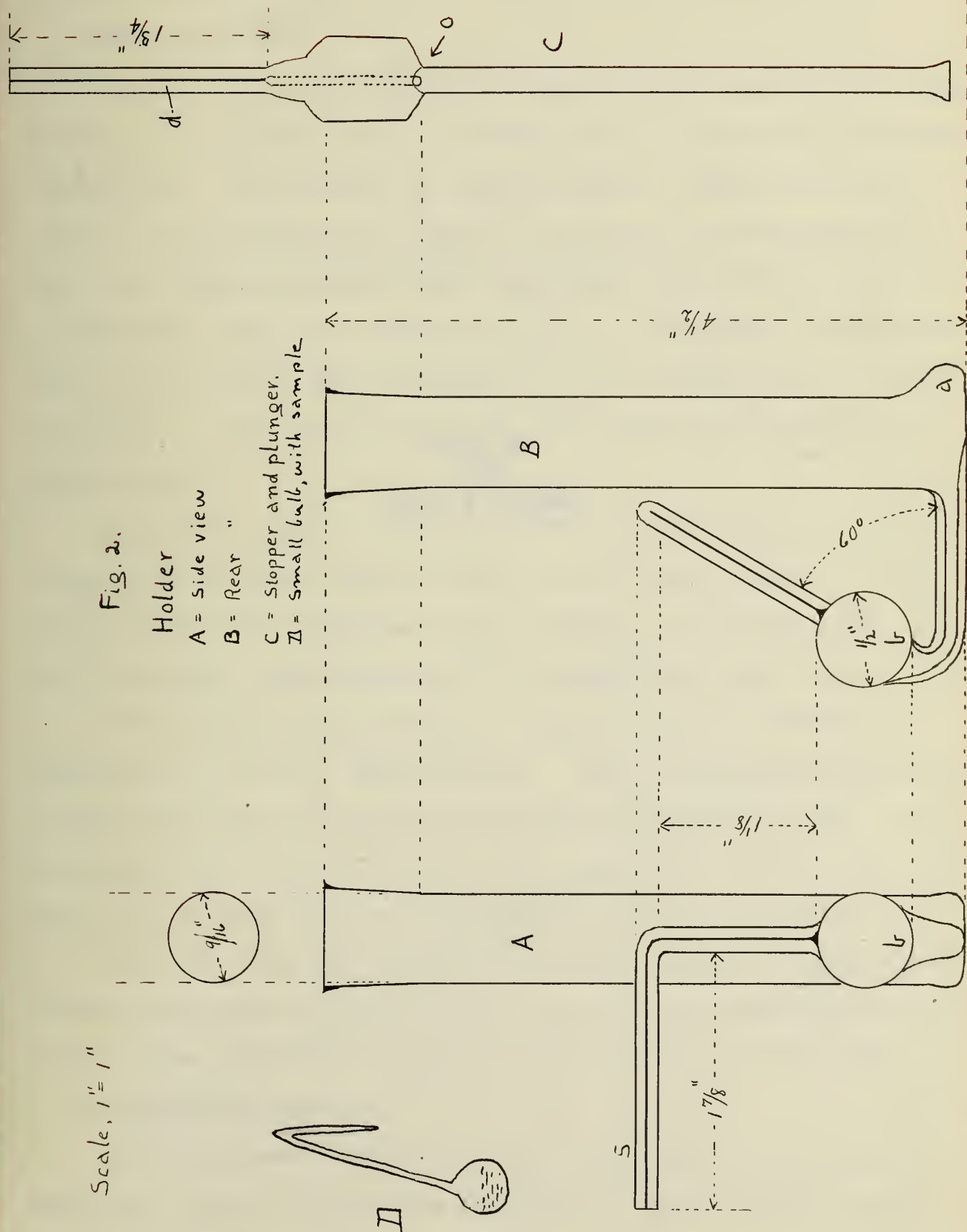
A = Side view

B = Rear "

C = Stopper and plunger.

D = Small bulb, with sample

Scale, 1" = 1"



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in no way interfering.

Combustion Tube:

No definite record was kept of the actual volume of air used during the combustion and for sweeping out the apparatus for determinations, 1-3; however, it was very small, indeed compared to that in No. 4, particularly in regard to the amount used after combustion for sweeping out the whole apparatus. It will be noted that a far better value was obtained in No. 4; this caused the abandonment of the quartz tube, mentioned in the Introduction, for one of 1/4" bore. This size was used in all combustion determinations thru No. 207.

Beginning with No. 45, and up thru No. 108, nearly all the combustions were run two at a time, in the same furnace. Fig. 3 indicates how the two tubes were arranged; a cross-sectional, top view is shown. Non-transparent Vitreosil tubes were used.

The holders were attached at 3 and 4, and the absorption apparatus at 1 and 2, respectively. The two associated combustions in each case are indicated in the tables by grouping them. For instance, 45 and 46, 47 and 48, etc., were run at exactly the same time, in the same furnace and hence, at the same temperature.

From No. 4 up thru No. 54, the entire length of tubes was 22 inches; from there on up thru No. 108, 42 inch tubes were used, the latter since a 30 inch furnace was used instead of a 12 inch.

Absorption Apparatus:

As in the case of the holders, so also with the absorption apparatus, several types were tried out. Here success was met

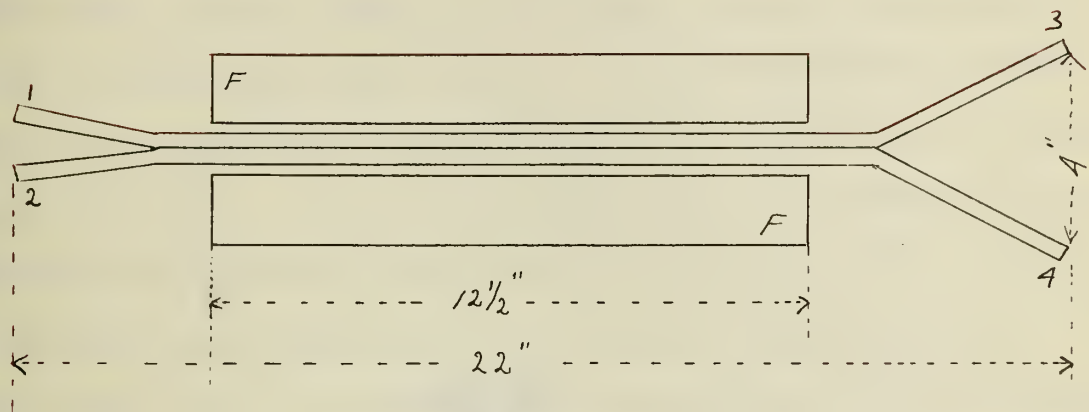


Fig. 3.

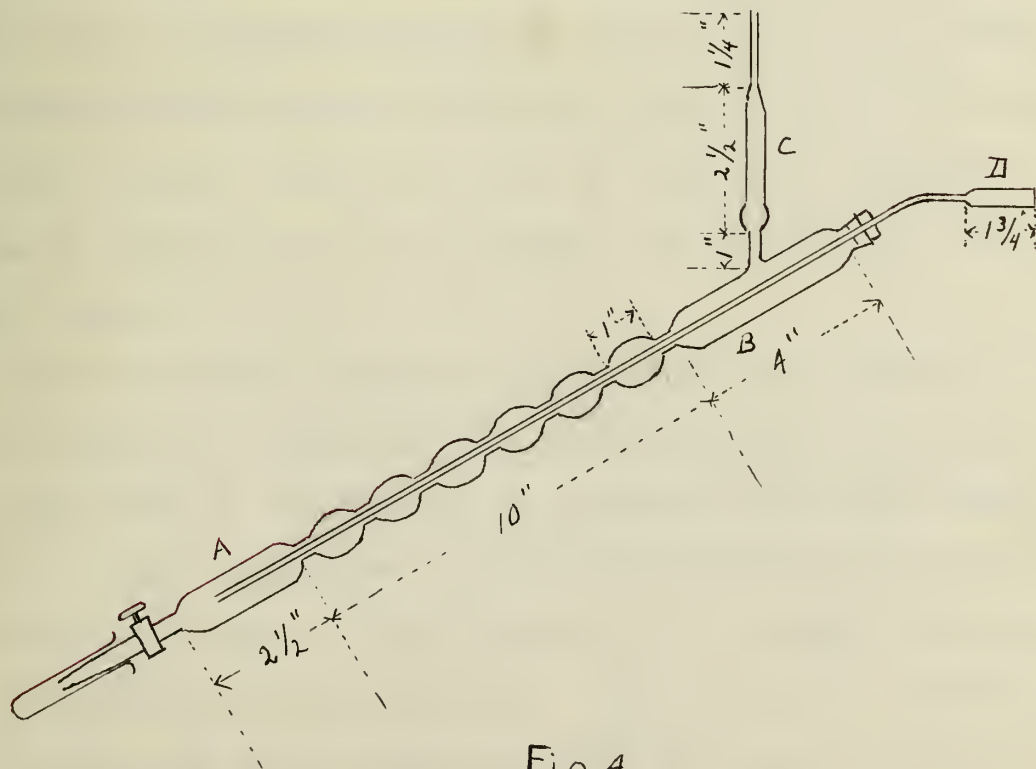


Fig. 4.

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earlier and beginning with determination No. 1 and up thru No. 108 the style used is indicated in Fig 4. Some very early experimental work on absorption apparatus, in which modifications of U-tubes, etc., were used, has not been recorded in this paper.

With the central tube, D, withdrawn, and with the apparatus inclined at the angle shown, 10 cc. of sodium sulphite solution are allowed to run down into the lower part, A; then 25 cc. of sodium hydroxide solution. It will be noted that this places the greatest concentration of sodium sulphite at the lower end of D; the idea being to make more certain the prevention of oxy-compounds.

The side arm, C, is packed with glass wool, which is soaked with a portion of the above mentioned 25 cc. of sodium hydroxide.

Both reagents are measured by means of pipettes.

The central tube, D, is now inserted and the rubber stopper made tight. The upper end of D, has about the same bore and wall thickness as the quartz combustion tube, so that when butted against the exit ends, 1 and 2, of Fig. 3, and held firmly with a heavy piece of rubber tubing, the passage way from quartz tube to glass is almost perfect.

Gentle suction applied at the end of the side arm, C, causes the products of combustion and decomposition in the quartz tube to be drawn down D, and then to be bubbled up thru the absorption solution. The liquid rises, partially filling the part B, but does not reach the level of the side arm, C. A small air space is left in the upper part of each bulb. The suction is such that about 80 to 100 bubbles per minute form at the lower end of D, the small

bore part being about 2 mm. Care must be taken that the annular space between the outer wall of the small part of D and the inner wall of the tubing between the bulbs is about 1 mm. or slightly more. If much less, the absorption solution will be drawn up entirely into B; while, if too large, the upper bulbs will not fill up, the solution remaining in A and the next two or three bulbs.

When in operation, the absorption apparatus is held at an angle as shown, about thirty degrees.

The small test tube, slipped over the tip of the glass-cock, catches any drops, which may leak out and be lost.

At the end of the run, the rubber connection at D is removed, the absorption apparatus suspended vertically, and the solution allowed to run into a 500 cc. Erlenmeyer flask. Then D, on being removed, is washed inside and out. A few successive small portions of wash water allowed to run down thru the apparatus suffice to wash it out completely. Of course, the side arm is also washed out. Completeness of washing should be tested in each case.

Furnaces:

During the first 54 determinations a twelve-inch, electrically heated, Hoskins furnace was used for heating the combustion tube. This is indicated in Fig. 1 in the Introduction, and also in Fig. 3, Part III. A longer combustion furnace was needed and also a bomb furnace for use in Carius determinations. These were designed and built by the writer.

Combustion Furnace:--

This is shown in Plates Nos. 2 and 3. All dimensions given

are drawn to scale.

Briefly it consists of a piece of six-inch pipe with caps screwed on each end, and in the center of the pipe is supported an alundum tube which is electrically heated by the resistance wire wound upon it.

The alundum tube is centered by two flat iron rings, b, one at each end. This is shown in Figs. 2 and 3, Plate No. 2, each ring being held in position by three small machine screws. To make it possible to remove, or place on, either six-inch cap, without screwing, which might fracture the alundum tube, each cap was cut thru at the point, n, see Fig 3, Plate No. 2, and then fastened on again by means of the two machine screws, e-e, shown in Fig 2, Plate No. 2.

The six-inch pipe, with the two caps, core etc., is supported on two brackets as shown in Fig 2, Plate No. 2. These are made of 1/4" x 1" soft steel bar. The pipe is held securely in position by two machine screws, one at each end. See, m, Fig 2, Plate No. 2.

To make more perfect the heat insulation, the six-inch pipe and ends are covered with the regular asbestos pipe covering, which makes the total outside diameter about 9-1/2", and the length about 33".

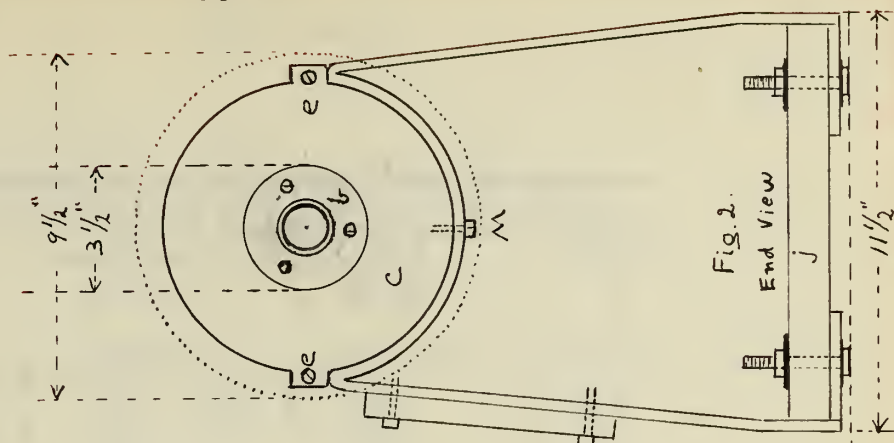
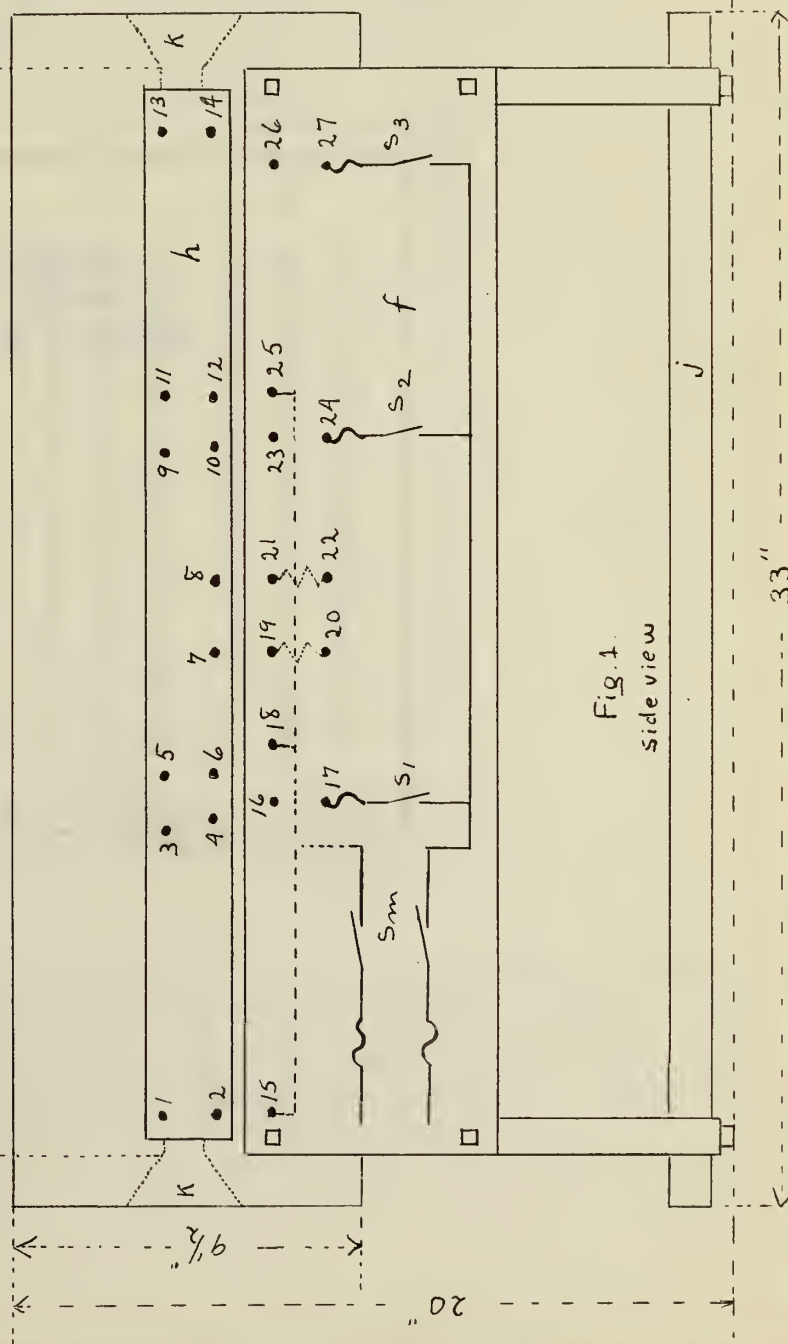
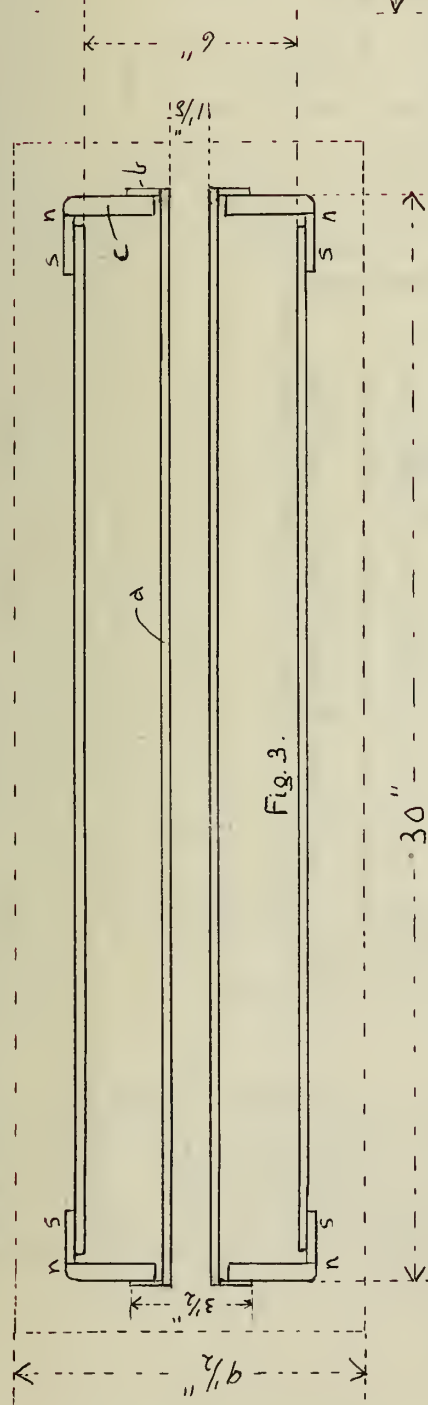
As shown in the diagrammatic sketch in Plate No. 3, Fig. No. 1, three separate sets of heating units are wound upon the alundum tube, each one covering one third the length or nearly ten inches. Each heating unit consists of two 45-foot coils of No. 20 Chromel A wire. The wire was first wound upon a 1/4" mandrel, and then stretched out carefully to such a length that the two coils in each

Plate No.2

Combustion Furnace.

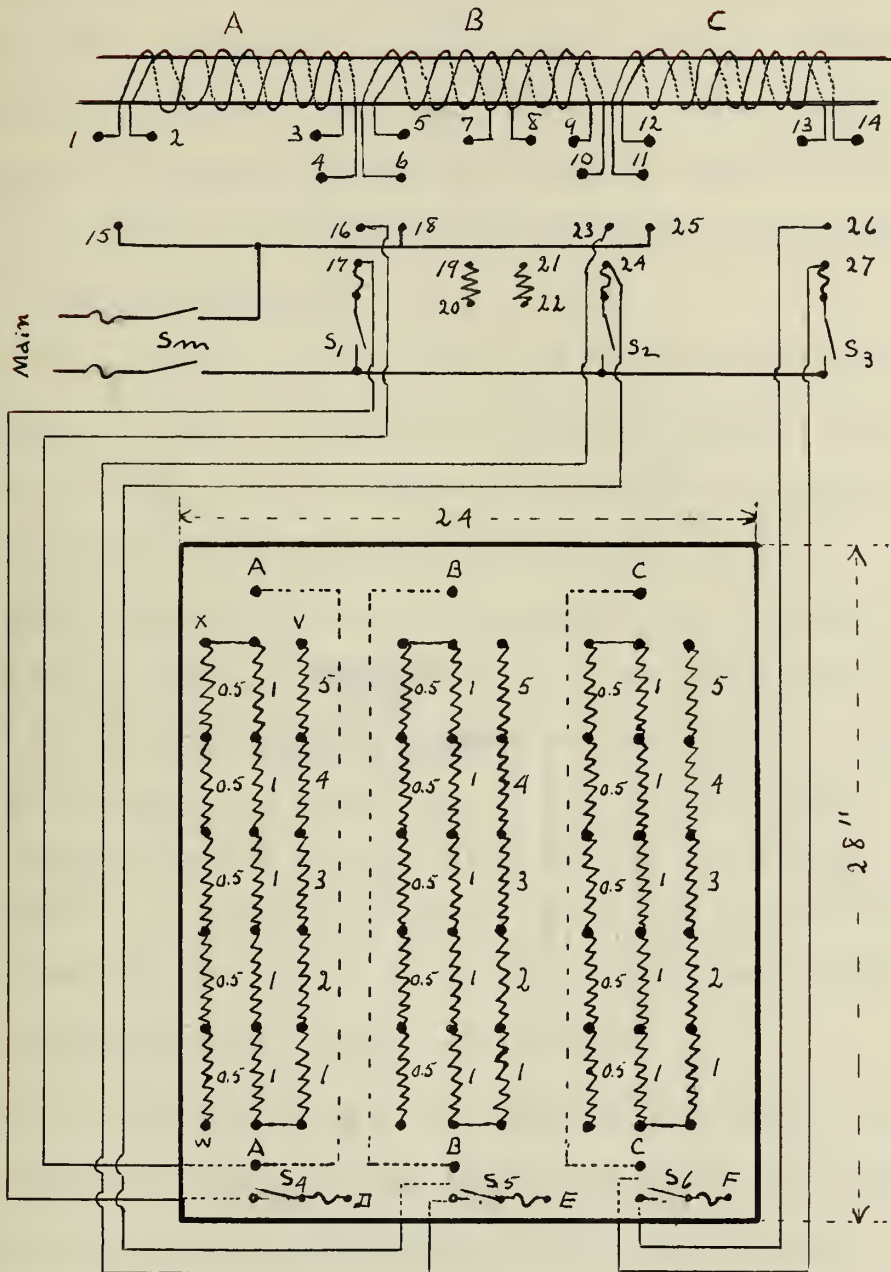
Scale, $\frac{3}{16}'' = 1''$

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34
Plate No. 3



To heat section, A, of the furnace: Join 1, 2 and 15; and 3, 4 and 16. Put some resistance in series between A and D (on the resistance board). See that the fuse at 17 is not over six amperes. Close main line switch and then the small ones S₁ and S₄. This is using the two heating coils in parallel. Similar connections for the other two sections, B and C.

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section, A, B and C, when wrapped around the alundum tube brought the free ends where wanted and also left a safe insulating space between the surfaces of each coil itself. Care was also exercised to see that the spaces between the wire of each coil were fairly uniform, in order to prevent over heating in spots; otherwise, the wire is likely to burn out.

At the boundary between A-B, and B-C, and also at the outer extremities of A and C, there are rings of transite board, firmly cemented in place, and to these are fastened the ends of the coils, the wire passing through three small drilled holes.

To make possible the easy hinging out of the ends of the coils to the binding posts, indicated by dots on the board, h, see Fig. 1, Plate No. 2, also in the diagram sketch, Fig. 1, Plate No. 3, a 25" x 4-1/4" strip was sawed out of the six-inch pipe. This open space lies back of and partially above the insulating board, h, Fig. 1, Plate No. 2. The free ends of the coils are insulated from the holes in the six inch pipe, thru which they come to their proper binding posts, by small clay pipe stems.

When all the coils were in position and before inserting the core, with its mounted coils, within the pipe, they were entirely covered with alundum cement which was allowed several days to dry out and then current, sufficient to heat the coils quite hot, was passed thru them.

The core was then placed in position, and the free ends of the coils with their insulating clay pipe stems were covered with alundum cement. The latter was also allowed to dry out and then was baked by passing current thru the coils.

A removable strip of sheet iron was then screwed over the cut-away side of the six-inch pipe.

The furnace was now set upon one end, the upper disk taken off by removing the screws, e-e, Fig. 2, Plate No. 2., and the vacant space between the core and the inner wall of the pipe carefully packed with the insulating material, known by the trade name of Sil-o-Cel. The disk was then fastened on, and furnace set upon the other end, etc., and the Sil-o-Cel tapped in at that end.

The pipe, with core, etc., was then bolted in position as shown in Fig. 2, Plate No. 2.

The board, h, is about 3/16" thick, insulated from the iron pipe by a 3/8" layer of asbestos board, to prevent scorching, and held in position by three small machine bolts; the latter are not shown in the drawings.

For binding posts, those salvaged from the common dry batteries were used. The numbering of all binding posts in Fig. 1, Plate No. 2, corresponds exactly with that in Fig. 1, Plate No. 3.

In Fig. 1, Plate No. 2, f, is a 7/8" pine board on which are mounted the three small switches for the sections A, B and C, and also the main line switch, fuses, and other necessary binding posts.

At the bottom of the Plate No. 3, directions are given for making the proper connections in order to heat up any one, or all three sections of the core of the furnace.

If one wishes to heat only one half of the middle section, say the one toward C, the following connections should be made, providing one wishes to use the heating coils in parallel: Join 18,

20 and 22; 19, 21, 7 and 8; and 9, 10 and 23. Now set some resistance between B and E in Fig. 2., Plate No. 3; close the main line switch S_m and then the small switches, S_2 and S_5 . Of course, a fuse not larger than six amperes should be at 24.

The connections 19-20 and 21-22 bring into the circuit two auxiliary resistance coils, suspended underneath the furnace. Each consists of 21 ft. of No. 20 Chromel C, whose resistance matches well the resistance of that part of the heating units in section B, which is not being used. The resistance used on the controlling board, Fig. 2., Plate No. 3, is then set for practically the same position as though the whole of section B were being heated.

The construction of the controlling resistance board, Fig. 2, Plate No. 3, is as follows:

A back board 24" x 28" was covered with asbestos paper and across this, evenly distributed, are fastened, six wooden strips, 5/8" x 5/8", on which to mount binding posts, indicated by the dots. Between the binding posts, as shown, is stretched some resistance wire of such a length as to give a resistance, which is marked to the right of each individual section of the resistance. Thus, if the A (either one) binding post was connected to x, and D to w, the resistance which would be brought into series would be 2.5 ohms. If A were connected to w, and D to v, then a total of 22.5 ohms would be involved. Of course, many other connections may be made, not only in series, but also in parallel, and so is afforded considerable variability between zero and 22.5 ohms. Connections are made by means of flexible lamp cords.

The following is some data recorded upon performance (using the coils in each section in parallel).

Heating Apparatus to 900° C			
Time	Temperature	Current for each section (amperes)	Resistance for each section (ohms)
2:22	room	6.20	1.5
2:38	395° C	6.15	1.5
2:56	660°	6.10	1.5
3.17	900°	6.10	1.5

To maintain each section, A, B and C at a temperature of about 900° C., using the coils in each section in parallel, the following was recorded:

Coils	A	B	C
Resistance in series (ohms)	12.5 - 14.0	15.5 - 17.5	12.5 - 14.0
Current (amperes)	3.5 - 3.7	3.2 - 3.6	3.5 - 3.7

The varying is the result of an unsteady line voltage, which at times changed 10%.

The following will indicate about the current and resistance required per each section to obtain certain desired temperatures.

Time	Temperature	Current (amperes)	Resistance (ohms)
2:45 P.M.	640° C	2.6	22.5
3:15	640°	2.6	22.5
4:00	640°	2.6	22.5
4:00	640°	3.5	13.5
5:20	780°	3.5	13.5
5:50	815°	3.5	13.5

5:50 P.M.	815° C	3.0	19.0
7:00	790°	3.0	19.0
7:00	790°	3.25	16.5
7:45	810°	3.25	16.5
7:45	810°	3.50	13.5
9:15	815°	3.50	13.5
9:15	815°	2.5	22.5
next morning	725°	2.5	22.5

To obtain lower temperatures one may, of course, use only a single coil in each section, or two coils in series, etc. No data on this matter was collected.

The above described furnace has seen many hours of service at 900° C and yet shows no signs of deterioration.

The alundum tube used in the construction of this furnace was manufactured by the Department of Ceramic Engineering, University of Illinois.

Bomb furnace;--

This is shown in Plates Nos. 4, 5 and 6. All dimensions in 4 and 5 are at the scale given.

In brief, this consists of six two-inch iron pipes bound together by means of three iron bands, and around approximately one half the length of the bundle of pipes and well electrically insulated from them are wound several heating coils. There is also a heating element located in the center. A 1-1/4" iron pipe, holding the bomb, is lowered by means of pulleys suspended from a square framework of four pipes supported overhead and a counter-

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.Biography

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VI. Summary

4. Analysis

c.

A C K N O W L E D G E M E N T

To Professor George McPhail Smith, under whose direction this investigation was carried out, the writer wishes to express his gratitude for the many kindly suggestions which he offered.

He also wishes to thank Doctor George Denton Beal for his kind assistance in proof reading given in the absence of Professor Smith; Professor David Ford McFarland for suggestions on electric furnaces; Professor Ralph Kent Hursh for the alundum tube, manufactured under his direction; and Mr. Paul Anders, who made all the glass and quartz apparatus used in this investigation.

H. A. Van Winkle.

• I N T R O D U C T I O N

Shortly after our entry into the Great War, the Department of Chemistry of the University of Illinois received a request from the United States Bureau of Mines for a rapid, approximate method for the analysis of chlorpicrin. Professor George McPhail Smith took up the work immediately and shortly suggested the scheme, which is indicated in Fig. 1.

The sample, introduced from a weighing burette into the small Claissen flask A, was drawn thru the heated quartz tube C-C, of 7/8" bore, held at a temperature of 950° C., by means of the twelve inch Hoskins electric furnace F-F, and the products of decomposition and combustion absorbed in 10% NaOH solution in flask B. The suction was obtained by means of a water pump, and was so regulated that the slight fog, which appeared in B, did not rise much above the surface of the liquid. To prevent any possible escape of HCl and Cl₂, the residual gases were drawn out thru the glass wool, held in the side arm of B, which was soaked in 10% NaOH solution.

After the sample in A was volatilized and after due care to sweep out the apparatus, the contents of flask B were carefully washed out into an Erlenmeyer flask. Metallic zinc was then added and, after boiling for a short time, the solution was acidified with dilute sulfuric acid, and then the boiling continued to the complete solution of the zinc. The halogen was then estimated by the Volhard method.

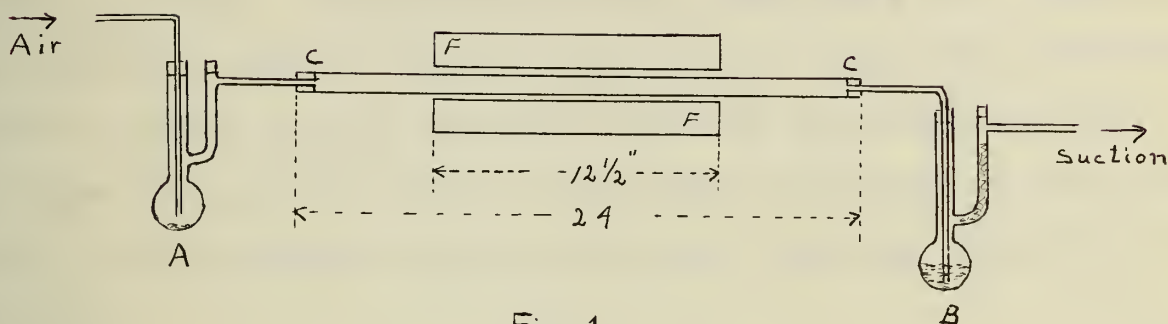


Fig.1.

The following data were recorded:

Temperature of furnace	950° C.
Absorbing solution	25 cc of 10% NaOH
Sample taken	0.2717 grams
Weight found	0.2646 grams ¹
Percentage of theory	97.3% ¹
Approximate time for determination	About one hour

¹ Based on chlorine content

In view of the present methods which are available for halogen determinations in organic substances, it was suggested to the writer that he follow up the above work and ascertain whether the scheme had a wider application, particularly to volatile, organic, substances.

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II

Present Methods

The methods which have been proposed for the determination of halogen in organic compounds may be discussed under the four general headings: double decomposition, splitting out, reduction and oxidation, these in turn, in some cases, being again subdivided. In what follows, some of the more important outstanding methods that have been proposed will be discussed; to include all that one finds in the literature would involve more time and space than is warranted.

Double Decomposition:-

Wet Treatment:

There are a few organic halogen compounds, such as α -substituted ethers, ketones, acids and esters, which in water alone or with a water solution of sodium or potassium hydroxide, yield solutions in which the halogen is ionized. Meyer based his method of analysis of acid chlorides upon that fact.¹ The amine salts of the halide acids may usually be determined directly. The halides of the radicals allyl and benzyl give up their halogen in basic solutions; also when a nitro group is ortho or para to a halogen on the nucleus, the latter may usually be removed with alcoholic potassium hydroxide.

In some cases of aromatic compounds, with halogen in the side chain, also a few aliphatic alkyl halides, especially iodides, the halogen yields to a treatment of alcoholic silver nitrate.

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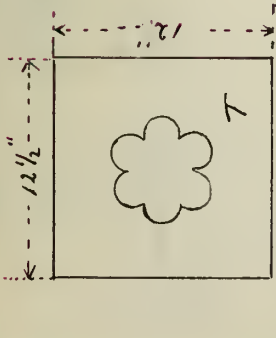


Fig. 2.

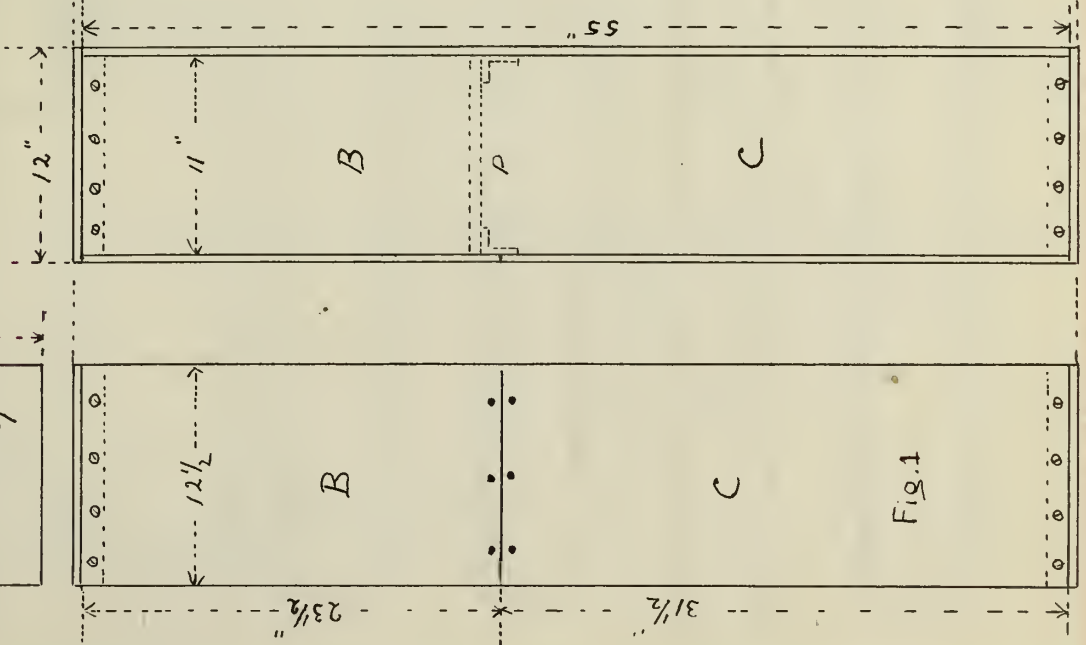


Fig. 1

Fig. 3

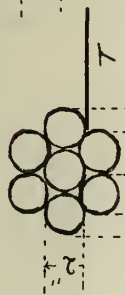


Fig. 6.

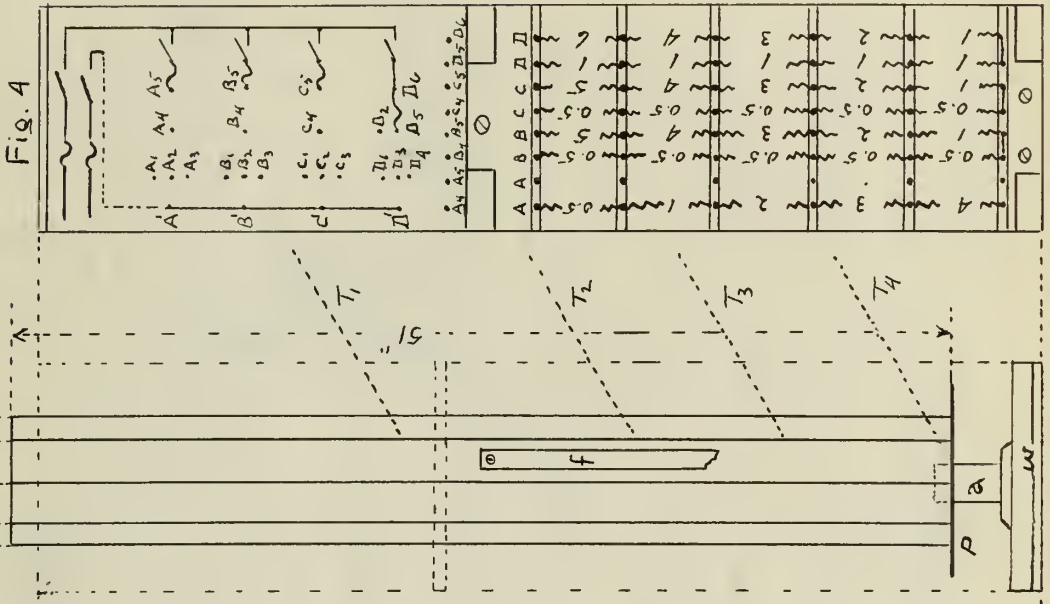
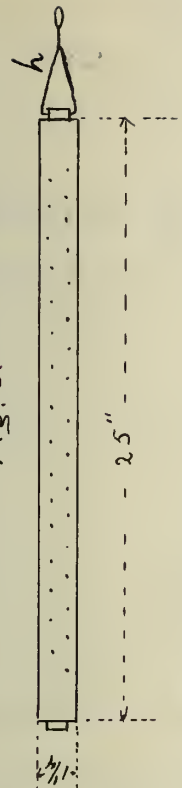


Fig. 4

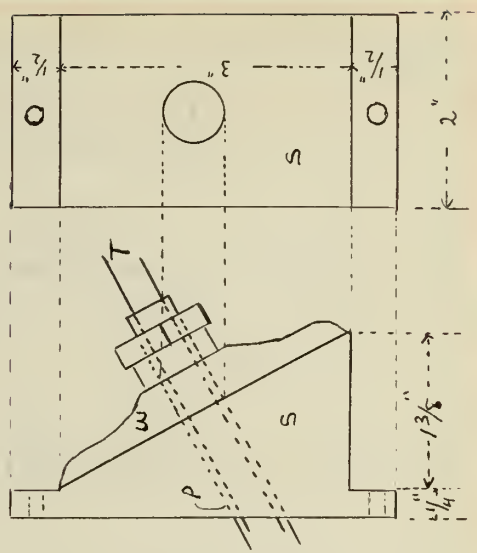
Plate No. 5.

Figs. 1, 2, 3 and 4, Scale, $\frac{3}{32}'' = 1''$

Fig. 5, Scale, $\frac{1}{2}'' = 1''$

" 6, " $\frac{1}{8}'' = 1''$

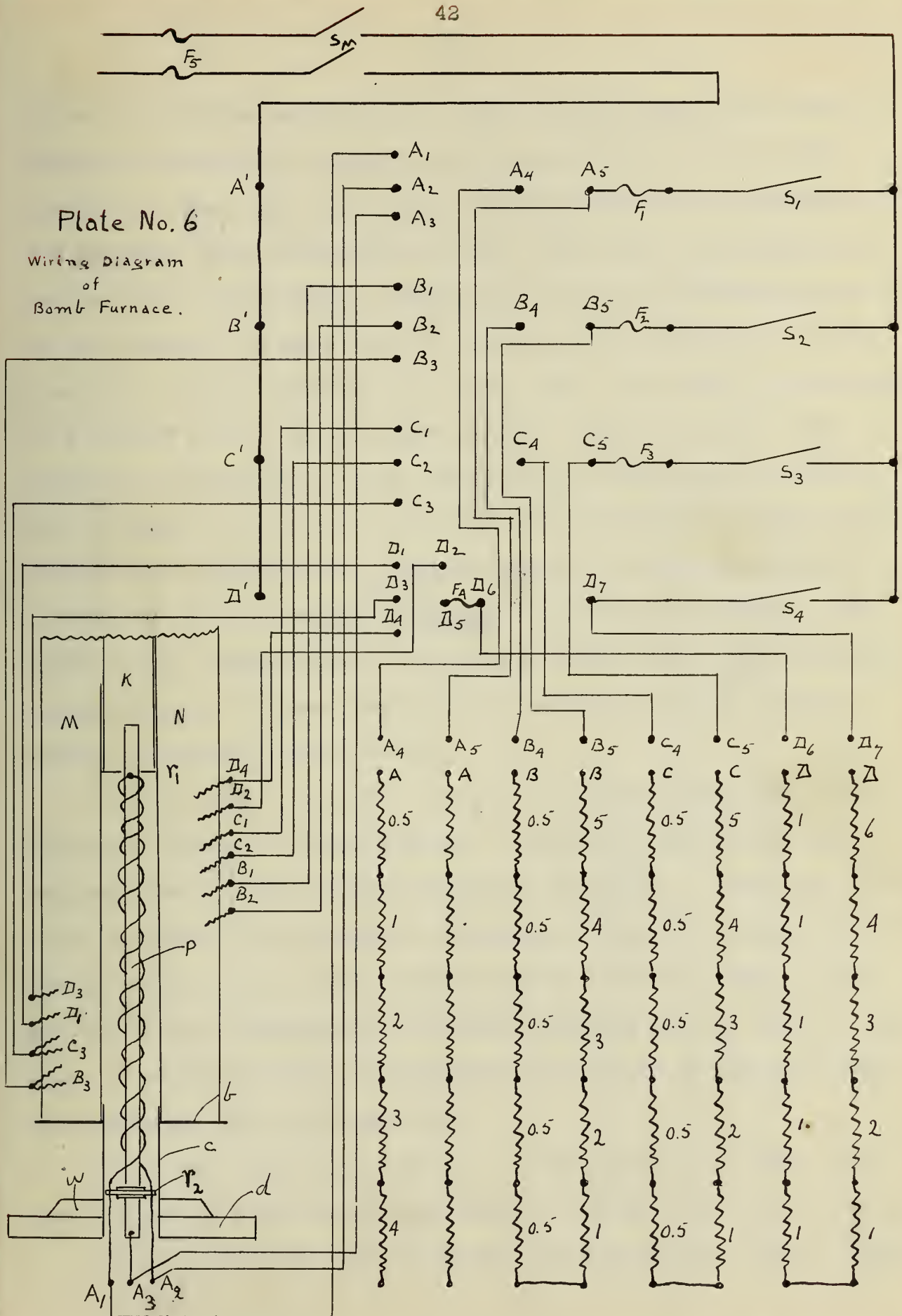
Fig. 5



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Plate No. 6

Wiring Diagram
of
Bomb Furnace.



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poise down to the heated zone of the two inch pipe; the latter stands in a vertical position and is heated only at the lower portion. Thus, six bombs may be introduced into or withdrawn from the furance, each independent of the other; also the furance may be operated continuously. That the change of temperature may not be too sudden, the bomb and its casing may be lowered or raised gradually a short distance at a time, etc. The whole is encased in a 12-1/2 x 12 x 56" box made of 1/2" transite board. The interior is divided into two compartments, see B and C in Figs. 1 and 2, Plate No. 5., by a partition made of transite board, see p in Fig. 2., Plate No. 5. The heating coils wound around that portion of the six two-inch pipes in the lower compartment are covered with asbestos paper glued with water glass, and then the remaining space between the asbestos covering and the outside casing is packed with Sil-o-Gel.

In Plate No. 4 is shown a front elevation, minus the switch board and controlling resistances. Also only one of the six counterpoises, with necessary pulleys, is shown. The board to the left, A, should lean slightly backward so that the weights will not easily swing out of their proper grooves. To the right, D is a guard for the thermometers to prevent bumping against them. The lamp, L, with its shade, illuminates the scales of the four 350° C thermometers, T₁, T₂, T₃ and T₄.

Plate No. 5 and also the part of the drawing in lower left hand corner of Plate No. 6 give some of the details of construction.

The six two-inch iron pipes are grouped around a small length

of two-inch pipe, a, in Fig. 3, Plate No. 5, and rest upon the iron plate P, the space between the latter and the wooden planking, w, being filled with several layers of asbestos board, which not only prevent the iron plate from slipping down to the floor flange, but also prevent the scorching of the planking when the furnace is in operation.

There is an eighth piece of two-inch pipe, which is indicated only by the circle in the group of seven, at the top of Fig. 3. This pipe extends downward as far as the partition, P, shown in Fig. 2; see also K in Plate No. 6. This pipe has both ends blocked with plugs, which, when screwed in, are flush with the edge of the pipe. Then on top of these ground off plugs are fastened discs, made of thin transite board, whose circumference is at all points in touch with the surrounding six two-inch pipes. This shuts off six triangular air passages.

On the inner side of the top and bottom pieces of the transite board box there is to be found 1-1/4 inch planking; which makes it possible to fasten the whole together with wood screws.

In Fig. 3, Plate No. 5, f, is a part of one of the six narrow one-inch strips of transite board, by means of which the outer heating coils are electrically insulated from the bundle of six-inch pipes. Thus very little heat insulation is interposed. These strips extend along practically the whole length of the pipe within the compartment, C, and are fastened on at each end with small machine screws, which are covered with a couple of layers of asbestos paper for electrical insulation. The heating coils are

cemented in place so that they can not slip out of position and make contact with an adjacent coil.

In Fig. 6, Plate No. 5, is shown one of the six 1-1/4" iron pipe casings for holding the bomb when it is within the furnace. The two plugs, machined down and threaded upon a lathe so that they would screw into the 1-1/4" pipe, which thus avoids the use of a union, and in turn, pipes larger than two inch, can easily be turned with the fingers. The wire running over the pulleys, indicated in Plate No. 4, is fastened to the spring hook, h, which can easily be spread apart by the fingers. It fastens into a small 1/8" hole drilled thru the nut of the plug.

To avoid the action of the concentrated nitric acid upon the iron pipe, in case a bomb explodes, a spoonfull or so of lime is introduced, followed by a wad of glass wool, before the plug in that end is screwed in. (The writer made a small wooden frame for supporting the pipe in a slightly inclined position while inserting the bomb, etc. The same was found convenient when opening up the bomb, etc.). The double row of dots in Fig. 6, represent 1/8" holes which permit the pressure of gas to reduce itself in case a bomb bursts. However, no ~~glass~~ escapes.

In Fig. 5, Plate No. 5, is shown how, by the use of the wooden block, s, and the small floor flange, w, the thermometers, with the protecting 1/4" pipe, p, are held in place. The inner end of the pipe, p, is up against the two-inch pipes, which thus permits the bulb of the thermometers to stand practically midway between the outer and inner heating coils.

In the lower left hand corner of Plate No. 6, are given some details of the inner and outer heating coils.

A $3/4$ " pipe, P, was wrapped with three layers of asbestos paper and then around it were wound two resistance coils, which are joined together and to the $3/4$ " pipe at the upper end, while the other two ends of the coils are free and come out thru the insulating ring r_2 , held in place by a nut on either side. The other end of the pipe is also insulated, since it rests in a hole cut thru the sheet of transite board; the hole in the plug in the two-inch pipe being larger than the one in the transite board. If the bottom $12-1/2$ " x 12 " piece of transite board is removed, this $3/4$ " pipe and its mounted coils can be withdrawn. The coils were cemented in place with alundum cement and then the latter baked by the current after the cement had dried out.

There are two double and two single ^{outer} heating coils. By a double coil is meant one which has the ends of two coils joined within the furnace, as is the case of those in the center of the furnace. Thus the ends of coils B_1 and B_2 are joined at the other end at B_3 ; similarly for C_1 and C_2 at C_3 . But the other ends of D_1 and D_4 are not joined. The ends of the coils within the furnace are properly labelled.

These outer coils are wound closer together near the bottom of the furnace with the hope that this would result in a gradual falling off of the temperature as one goes upward. This was not quite realized, as will be shown later.

The coils had been wound upon a mandrel, etc., as in the con-

struction of the combustion furnace.

The resistance board and the switch board, with their numbering and lettering, showed in Fig. 4, Plate No. 5, correspond exactly with that given in the digrammatic drawing of Plate No. 6.

The construction of the resistance board is on the same principle as given in the description of the one for the Combustion Furnace.

If one wishes to use coils A_1 and A_2 in parallel, join A' , A_1 and A_2 ; and then A_3 and A_4 . Now place in series some control resistance across A_4 and A_5 . Then close the switches S_m and S_1 . (It will be noted that the $3/4"$ pipe, upon which the inner heating coils are mounted is part of the circuit in this case).

To use A_1 and A_2 in series, join A' and A_1 ; then A_3 and A_4 . From here on the procedure is the same as that just given, using the coils in parallel.

To use B or C coils in parallel, or series, the connections are similar to that given for the A coils.

The D coils are not connected within the furnace, nor is the switch S_4 , the same style as the other three small ones. (Only three small switches of like type were available and so an odd one had to be used. This necessitated the use of extra binding posts.) If one wishes to use one of the D coils, alone, make the following connections: Join D' and D_1 ; D_2 and D_5 ; then close switches S_m and S_4 . The control resistance would be cut in across D_6 and D_7 . For the other D coil, alone, join D' and D_3 ; then D_4 and D_5 , etc. The writer would not advise the use of the D coils in parallel,

since the current would be too high. In series, the connections would be as follows: Join D' and D₂; D₂ and D₃; then D₄ and D₅. Now close the switches, S_m and S₄. The control resistance is placed in series across D₆ and D₇.

The upper piece of transite board on the front side of the outer casing serves as a base for the switch board. It can be removed by taking out the proper screws and machine bolts, which are indicated by dots; see Fig. 1, Plate No. 5.

If one wishes to get at the outer heating coils, it would be best to lay the furnace on its ^{rear} side and then remove transite board serving as a lid for the compartment C.

The base of the resistance board, which consists of the transite board, is fastened on top of the lid just mentioned and can be detached from the furnace by removing the three machine bolts shown in Fig. 4, plate No. 5. In this case, the 5/8" x 5/8" strips, upon which the binding posts of the resistance board are mounted, were also made from transite. In the case of the resistance board, constructed for use with the Combustion Furnace, it was found that the binding posts becoming warm scorched the wooden strips and some of the posts loosened.

The inner two coils consist of 52 feet each of No. 20 Chromel A.

The outer coils had been cut for another furnace and so these lengths were used, no splicing being done. Each one of the B and C coils consist of 30 feet of No. 16 Chromel A; while in the case of each of the D coils, 16 feet of No. 16 Chromel A.

While the size of the wire in each coil will permit more



current than the writer used in the operation of the furnace, he would advise that the maximum current for any length of No. 20 wire be not over 3.5 amperes, and for No. 16, not over 4 amperes.

The relation between the current that will flow (on a 110 voltage circuit) and the resistance to be used in series when the A, B and C coils are being used in parallel, and the D coils in series, is indicated in the curves shown in Fig. 5 . The variability is due to the heating up of the coils, and the changing of the line voltage, which at times varied ten percent.

If the control fuses, F_1 , F_2 , F_3 and F_4 are of the proper limiting size, the above will be taken care of.

One may also use a heating coil as a resistor, and thereby conserve heat energy which otherwise might be lost.

The average resistance, as measured by the fall of potential method was found to be as follows:

Coil Combinations	Ohms
Either of A, alone	34.6
A ₁ in series	69.0
A ₁ in parallel	17.0
Either of B or C alone	7.0
B or C in series	14.4
B or C in parallel	3.5
Either of D, alone	4.35
D, in series	8.70
D, in parallel	2.17

If one wishes to heat up the furnace rapidly, use at the same time the A, B, C and D coils in parallel, and with such resistance

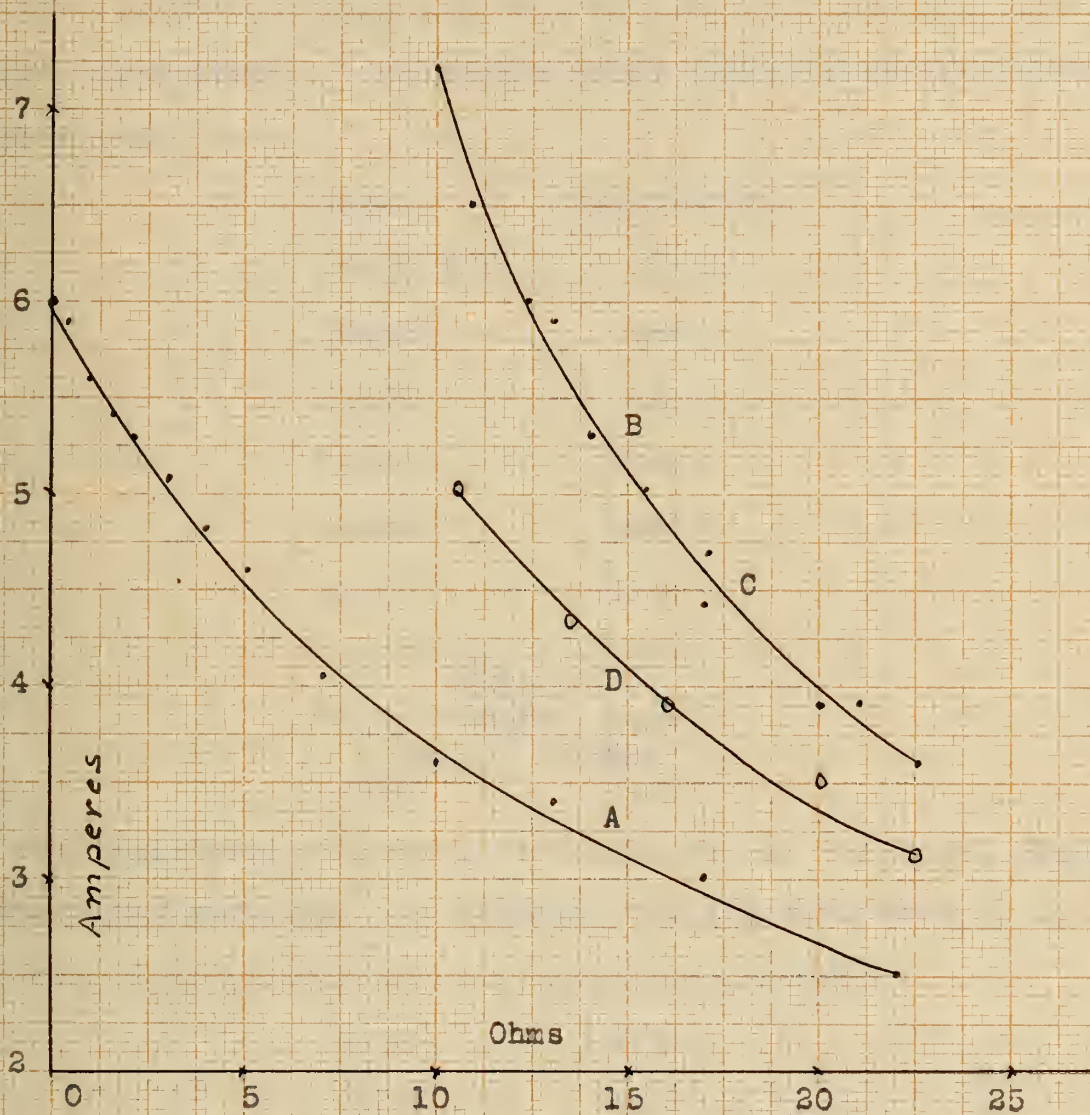


Fig. 5.

Curve A = Using A coils In parallel

Curve BC = Using Either B Or C Coils In Parallel

Curve D = Using D Coils In Series

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that the current per each set will be 6.0, 6.5, 6.5 and 3.6 amperes, respectively. On such a total combination the following was obtained:

Time	Temperature
10:30 A.M.	30° C
10:45	65°
11:00	85°
11:15	110°
11:30	140°
11:45	170°
12:00 noon	193°
1:00 P.M.	260°
2:00	315°

The resistance in series with each set of coils was changed at this point such that the current thru the sets were 3, 5, 5 and 5 amperes, respectively and the readings continued.

2:30	318°
3:05	318°
4:05	323°

From 4:10 to 4:15 the resistance was changed to the maximum available for each set, which is 10.5, 17.5, 17.5 and 21 ohms, respectively, and the readings continued.

8:00	285°
------	------

At 8:10 the switches S_2 and S_3 were pulled.

9:15	260°
------	------

All switches were then pulled and the experiment ended.

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The writer had hoped as previously stated that the highest temperature would be recorded on thermometer T_4 (See Fig. 3, Plate No. 5), and had wound the outer heating coils much closer near the base of the furnace, but it developed that the highest temperature was always read on T_3 , it being about 12-15° above T_4 and 22-25° above T_2 , when heating up the furnace. Since T_1 is not in the heating zone, it never reached much above 100°, even when the maximum temperature on T_3 read 300° C.

On two different occasions the A coils, in parallel and with no resistance in series, were left on all night and the next morning the readings of the four thermometers were as follows:

T_1	105 and 110° C
T_2	257 and 250° C
T_3	320 and 325° C
T_4	305 and 310° C

The current was about 6.0 amperes.

If A coils are used in parallel, with the D coils in series as resistor, the temperature upon T_3 will stand about 250° C. The current will be 3.7 amperes.

If the B coils are used in parallel with the C coils (series) and the D coils (series) in series as resistor, T_3 will not go above 240° C.

The following will give some idea as to what the reading upon T_2 and T_4 will be when T_3 records certain temperatures:

T_2	145	165	180	190	225	250
T_3	170	200	225	240	285	325
T_4	155	185	210	220	265	295

The above gives data only on a few of the very numerous combinations which are possible with the coils and resistances which are available. It is hoped that enough has been given to make it easy for one to work out safe combinations which will give the temperatures desired.

Temperature Measurement:

Since the line voltage varied about ten percent it was impossible to calibrate the resistance controlling the combustion furnaces for certain temperatures and so resort was made to pyrometers, which were left in the furnace during the combustion. Small base metal couples were tried out, but they were found to deteriorate too rapidly. A Platinum-Platinum Rhodium element became available, but the only milli-voltmeter at the writer's disposal was one whose maximum capacity was 5.5 millivolts, on which the deflection at 900° C was beyond the limit of the scale. However, by inserting 270 ohms in series (from a standard resistance box) a maximum deflection was obtained at a temperature of 1000° C (measured upon standard Platinum-Platinum Rhodium pyrometer), which just reached the upper limit of the scale of the 5.5 millivolt instrument. A blank piece of paper was pasted over its scale and then the temperatures recorded upon the standard pyrometer were marked upon the paper scale where the needle stood. The calibration was carried out for every 25 degrees, from a little below 400° C up to 1000°. No cold junction was used in connection with the 5.5 millivoltmeter, it being calibrated in position. In this way a very accurate reading pyrometer was obtained for use

throughout the rest of the work. Subsequent re-checking up showed no deterioration of the improvised apparatus.

Preliminary Analysis Of Chloroform:

Combustion Method--

The first 54 analyses of chloroform are recorded in Tables III and IV, and they are given because they cover the early efforts to perfect the apparatus being used.

While the values given under determinations Nos. 31 to 43, inclusive, are much better than those from 44 to 54, inclusive, yet it was felt that the holder being used in the latter was of a better design and a slight modification was introduced. Originally it was almost like that shown in Fig. 2. That the change was in the right direction is indicated in determinations Nos. 55 to 68, inclusive. See Table V.

Determinations 69 to 90 inclusive were made in order to ascertain the smallest volume of air necessary to sweep out the whole apparatus after the sample had been volatilized, since the element of time was involved. No runs were made using less than 100 cc., since the latter gave good values and the time required was very small.

Comparative Analyses By The Carius Method:-

As previously stated, the purpose of the earlier work was to perfect an apparatus which first of all gave consistent values; higher efficiency being of secondary importance. It was now desirable to ascertain by some standard method of analysis what values could be obtained for the sample of chloroform being used.

TABLE III

Analyses Of Chloroform
Sample A

Theory = 89.02% Cl

Temperature 900° C

Det.	Sample (gms.)	Vol. Of Air ¹		Time' (min) ²		% Cl Found
		During	After	During	After	
1	0.5521	---	---	32	20	87.16
2	0.4891	---	---	50	25	79.78
3	0.5270	---	---	71	60	86.60
4	0.5346	2000	10000	155	300	88.93
5	0.5958	1250	2450	60	30	87.99
6	0.5481	---	---	60	15	86.30
7	0.6672	1500	---	50	--	86.90
8	0.6931	2000	1000	50	35	86.30
9	0.7219	1250	1150	65	40	89.02
10	0.7803	1300	750	45	18	88.13
11	0.8172	750	---	65	28	88.70
12	0.8464	1050	---	90	--	88.20
13	0.3074	500	550	48	20	86.70
14	0.2052	600	600	25	20	88.10
15	0.2227	325	375	28	13	88.40
16	0.2293	500	300	30	15	89.02
17	0.2401	525	400	32	12	88.76
18	0.2252	400	400	38	15	88.57
19	0.2201	1250	500	36	24	88.57
20	0.1856	600	700	42	20	89.12
21	0.3392	600	400	40	10	88.28
22	0.2416	500	500	35	23	77.14
23	0.3881	350	400	35	23	64.40
24	0.2586	2300	1000	134	30	87.80
25	0.2596	350	350	45	17	87.50
26	0.2627	800	500	58	22	88.42
27	0.2516	500	500	45	20	88.53
28	0.2628	1100	500	85	25	88.44

¹ Only air was used during combustion and for sweeping out the apparatus. The volumes given are those measured over the water in the water aspirating bottles, at room temperature; correction to standard and dry conditions not being made. In determinations Nos. 1 to 12, inclusive, the absorption solution was made up to 250 cc. and 50 cc. portions taken for titration.

² Time during combustion was counted from the starting of the water pump till no more fog and clusters of bubbles appeared in part A, of the absorption apparatus; time after, from then on until the aspirating was stopped.

TABLE IV
Analyses Of Chloroform
Sample B

Theory = 89.02% Cl

Temperature 900° C.

Det.	Sample (gms.)	Vol. of Air		Time		% Cl Found
		During	After	During	After	
29	0.2517	550	450	42	18	88.24
30	0.2936	600	450	45	27	86.94
31	0.2278	680	500	47	20	88.79
32	0.2658	600	500	43	21	88.39
33	0.3121	550	500	49	36	86.60
34	0.2910	600	500	42	21	88.39
35	0.2370	950	800	67	30	88.38
36	0.2829	1250	800	76	32	88.39
37	0.2439	1100	850	56	29	88.54
38	0.2599	750	800	66	32	88.30
39	0.2629	725	825	52	52	88.90
40	0.2825	775	800	65	30	88.52
41	0.2356	500	800	50	38	88.47
42	0.2351	450	800	50	--	88.46
43	0.2400	500	850	50	50	88.53
44	0.2421	800	1600	35	62	86.63
{45	0.3086	900	1650	84	128	88.31
{46	0.3104	900	1650	78	122	87.67
{47	0.3378	1000	2100	73	115	88.37
{48	0.3127	550	2150X	53	70	88.12
{49	0.2693	1050	1050	72	96	88.53
{50	0.2648	900	900	72	43	84.90
{51	0.5482	975	550	60	50	87.26
{52	0.5060	950	650	60	50	87.93
{53	0.5154	475	925	67	30	86.07
{54	0.5442	600	900	75	37	87.37

Notes applying to Table IV:

Same remarks regarding volume of air and time, following Table III, apply to Table IV.

In determinations Nos. 51 to 54 inclusive, the absorption solution was made up to 250 cc. and 100 cc. portions taken for titration.

Sample B was analyzed by Carius and the values obtained are 88.75, 88.76 and 88.90% chlorine.

TABLE V

Showing Efficiency Of Apparatus And Minimum Volume Of
Air Necessary To Sweep Out the Entire Apparatus.

Analyses Of Chloroform
Sample C

Theory = 89.02% Cl

Temperature 900° C

Det.	Sample	Vol. of Air ¹		Time ¹		% Cl Found
		During	After	During	After	
55	0.4756	1150	3250	76	85	88.69
56	0.5452	1300	3000	81	72	lost
57	0.5398	1300	1100	80	20	88.70
58	0.5089	800	1700	80	50	88.45
{59	0.2270	600	2600	53	105	88.48
{60	0.2662	700	2600	58	100	88.47
{61	0.2485	700	1450	117	49	88.49
{62	0.2665	600	1500	57	60	88.67
{63	0.2357	500	1400	57	58	88.25
{64	0.2905	800	1500	60	54	88.45
{65	0.2734	550	1550	50	75	88.45
{66	0.2777	650	1400	58	50	88.51
{67	0.2487	600	1400	45	51	88.62
{68	0.2572	800	1400	56	42	88.67
{69	0.2673	700	1200	43	48	88.69
{70	0.2497	770	1200	42	44	88.67
{71	0.2557	550	1100	44	32	88.60
{72	0.2567	650	1100	49	24	88.54
{73	0.2798	650	1000	43	43	88.66
{74	0.2617	750	900	47	28	88.58
{75	0.2803	590	800	37	31	88.57
{76	0.2642	675	800	37	31	88.67
{77	0.2722	500	700	38	27	88.53
{78	0.2817	500	700	38	25	88.46
{79	0.2741	600	600	34	18	88.56
{80	0.2717	600	600	34	18	88.68
{81	0.2552	530	500	34	20	88.80
{82	0.2622	570	500	31	16	88.59
{83	0.2567	530	400	29	13	88.79
{84	0.2788	620	400	30	12	88.64
{85	0.2518	730	300	33	9	88.64
{86	0.2703	750	300	42	11	88.67
{87	0.2524	830	200	39	6	88.67
{88	0.2535	850	200	40	6	88.68
{89	0.2739	850	100	34	3	88.71
{90	0.2718	650	100	34	2	88.71

Notes following Table V:

Runs 55-58 2/5ths of absorption solution was taken for
analysis. Runs 59-90 all of absorption solution was titrated.

¹ See notes following Tables III and IV.

The Carius method was chosen in spite of some of its disadvantages, because values obtained are satisfactory. It was decided to continue this method of comparison in subsequent work, and so a suitable bomb furnace, already described, was designed and built by the writer.

The values obtained upon chloroform, sample C, are recorded in Table VI. The average, 88.44% chlorine, checks well with those values given in Table V.

The Effect Of the Variables:

Temperature:--

In order to determine the effect of increasing temperature upon the degree of decomposition, the series of experiments indicated below was carried out.

Temperature	% Chlorine found
900° C	82.82
800°	76.16
700°	60.85
600°	37.77

Chloroform, sample A, was used in these analyses.

Although the percentage of halogen obtained at 900° C was less than the amount actually present, this discrepancy was found to be due to faults in the apparatus and not to incomplete decomposition.

TABLE VI

Analysis of Chloroform, Sample C, by Carius
Method

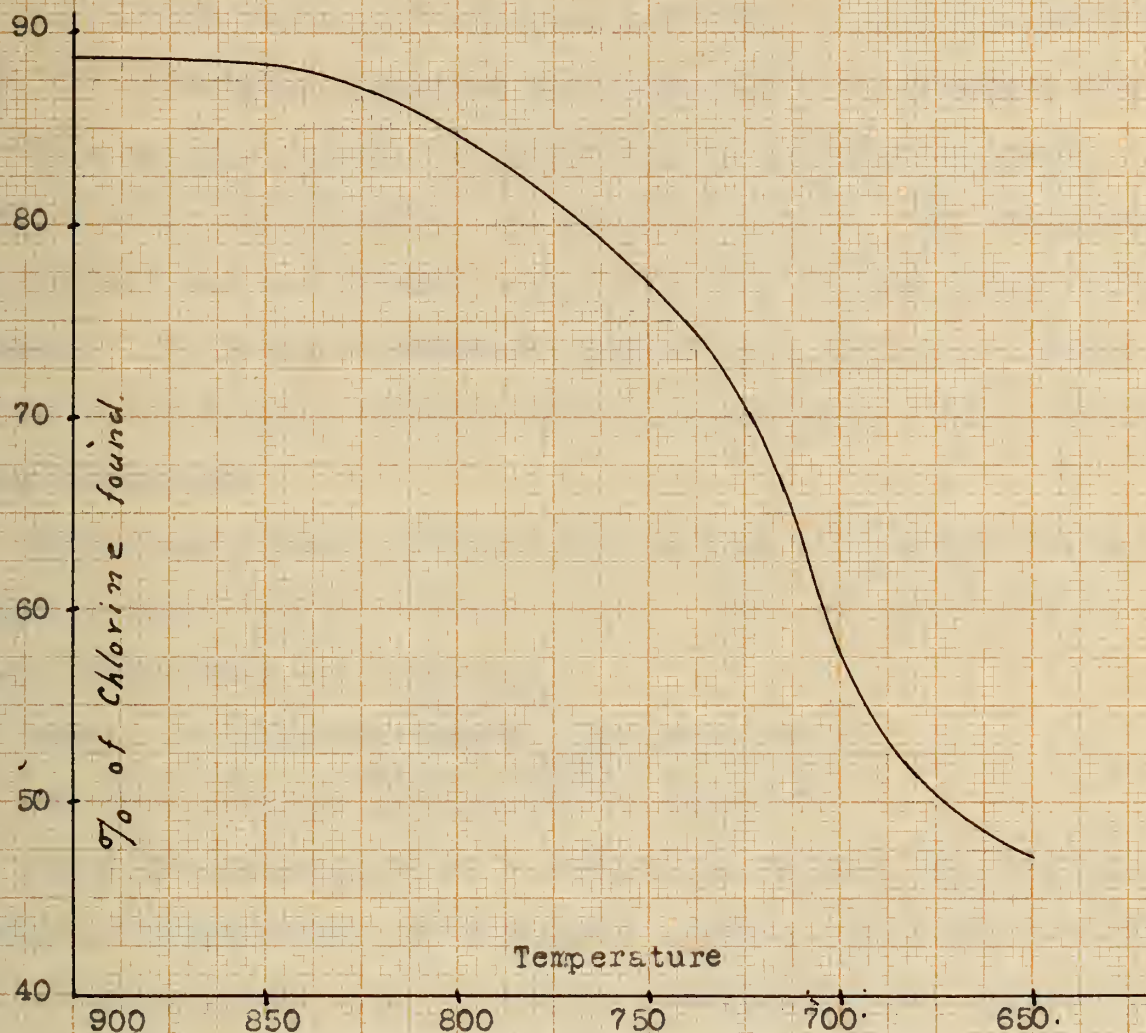
Determination	Sample Taken	% Chlorine Found ¹
91	0.2430	88.28
92	0.2485	88.20
93	0.2292	88.76
94	0.2449	88.48
95	0.2494	88.23
96	0.2888	89.19
97	0.2629	86.51
98	0.3004	88.39
99	0.3189	88.44
100	0.2508	90.25

¹ Average is 88.4% Chlorine, in
which determinations Nos. 96, 97
and 100 are not included

A second series of experiments to show effect of temperature on degree of decomposition is shown by the graph, Fig. 6.

Apparently at temperatures below 850° C the degree of decomposition of chloroform decreases rapidly.

At about 600° C, the temperature reached in a gas combustion furnace, with a glass combustion tube, an appreciable deposit of some fine needle-like crystals is found at the colder ends of the tube, especially if an insufficient amount of air is used for burning the chloroform.



To show effect of temperature

At	900° C	88.60% found
At	850° C	88.45% found
At	800° C	84.97% found
At	750° C	76.90% found
At	700° C	57.92% found
At	650° C	47.49% found

Using chloroform, sample C,
which by Carius method analyzed
88.40% Cl.

Fig. 6.

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The calculations on these runs referred to were not completed since the titrations indicated that they would be extremely low.

This material which is deposited is insoluble in water; slightly so in cold alcohol, but readily in hot. The recrystallized product was very fluffy, pure white and of fine needle-like crystals. It gives an excellent qualitative test for chlorine and was found to melt at about 229° C, corrected. This indicates hexachlorbenzene.

Since only a small quantity was on hand, the writer did not attempt a quantitative analysis of it. This indicated that a higher temperature was necessary.

Length of Heated Portion of Combustion Tube:-

The data obtained is recorded in Table VII.

Since the extremities of a combustion furnace fall off decidedly in temperature, the "lengths" given in the table are about 2 to 4 inches longer than the highly heated portion. Apparently when the length falls below 8 to 10 inches, low values may be expected.

Excess Air or Oxygen During Combustion:-

If one studies the data given for the first 54 determinations, he will conclude that the low values for chlorine were not due to an insufficient quantity of air during the combustion, but rather to faulty apparatus. Of course, unless an excess of oxygen is always present, charring in the combustion tube will result, and low values for the halogen will follow. This will be touched on later under Part V. If one sees to it that the ratio of air to volatile material does not suddenly change in favor of the latter,

TABLE VII

Showing Effect Of Approximate Length Of Heated Portion
Of Combustion Tube
Analyses Of Chloroform

Theory = 89.02% Cl		Sample C		Temperature 900° C			
Det.	Sample (gms.)	Vol. of Air During	After	Time (min) During	After	Approx. Length	% Cl Found
{ 91	0.2666	650	550	40	58	20"	88.42
{ 92	0.2704	850	550	42	59	20	88.74
{ 93	0.2624	550	500	42	19	20	88.47
{ 94	0.2460	550	500	44	19	20	88.32
{ 95	0.2866	685	500	56	18	20	88.47
{ 96	0.2625	900	550	53	28	20	88.43
{ 97	0.2539	600	500	34	17	15	88.68
{ 98	0.2619	600	700	17	17	15	88.90
{ 99	0.2749	550	500	36	17	15	88.46
{ 100	0.2678	600	500	36	13	15	88.75
101	0.2763	600	500	54	21	10	88.22
102	0.2685	650	500	47	18	10	83.71
103	0.2674	870	750	63	23	10	86.81
104	0.2551	600	500	43	18	10	lost

due to too excessive warming of the holder containing the sample, in an effort to help volatilize the material, the combustion goes smoothly and without much attention. The plan used was to place a thermometer beside the holder and then warm gently at a temperature from 10 to 30 degrees below the B. P. of the substance being analyzed.

A few runs were made using pure oxygen entirely, but no noticeable improvement in the chlorine values were obtained. These are not recorded in this paper.

Analyses Of Carbon Tetrachloride:

Combustion Method--

It was now decided to apply the scheme to the analysis of other substances. Carbon tetrachloride was chosen, mainly because its halogen content is so high. The results obtained are to be found in Table VIII

Carius Method--

These values are also recorded in Table VIII. Presumably the average, 92.37% chlorine is too high, since it is hardly to be expected that carbon tetrachloride would contain foreign matter with a chlorine content higher than its own. Possibly fragments of glass are involved.

TABLE VIII

Analysis Of Pure Carbon Tetrachloride, CCl_4

Theory = 92.20% Cl

B. P = 78°C

By Combustion							By Carius		
Det.	Sample	Vol. of Air		Time		% Cl	Det.	Sample	% Cl
		During	After	During	After				
{105	0.2594	630	500	55	20	91.84	109	0.2122	92.74
{106	0.2601	950	500	59	20	91.98	110	0.2321	92.50
{107	0.2578	650	500	57	19	92.00	111	0.2805	92.02
{108	0.2509	650	500	57	19	91.99	112	0.2208	91.94
							113	0.2813	92.63

Note: Determinations 105 and 106 - used 2/3 of heated portions of furnace or 20 inches; while in 107 and 108, used full length of 30 inches of furnace.

Analysis With Gas Heated Combustion Tube:-

Reasons For Abandoning The Electric Furnace:

Following up the work on carbon tetrachloride, the next substance used was ethyl bromide. The results were entirely unsatisfactory, the first four values obtained being 55.83, 63.02, 46.96, and 46.90% bromine. See Carius values in Table IX.

On investigation it was learned that the trouble was due to the heavy bromine vapors condensing in the combustion tube near the end of the furnace. To drive them over by warming would result in burning the rubber tubing holding the central tube of the absorption apparatus against the end of the combustion tube. Of course, in due time the bromine could be eventually drawn over by continued aspiration, or the furnace might be allowed to cool, and then the contents of the combustion tube washed over into the

absorption apparatus, but either of these procedures involved too much time.

It was decided to resort to a gas heated tube, providing a high temperature could be reached, since on turning out the burners, the tube would cool quickly and then it could be washed out.

Method Of Heating And Temperature Obtainable:

By placing a pair of Bunsen burners, with wing tops, set lengthwise of the combustion tube and using the hottest blue flame possible, it was found that a temperature of nearly 1000° C could be reached, particularly if an inverted V-shaped strip of asbestos board was suspended about an inch above the tube. Plate No. 7 shows the relative position of the burners, B, to the quartz tube, Q. No difficulty was found in maintaining the proper temperature.

Apparatus Used:

The entire style of holder, absorption apparatus and somewhat the combustion tube underwent a decided change at this point.

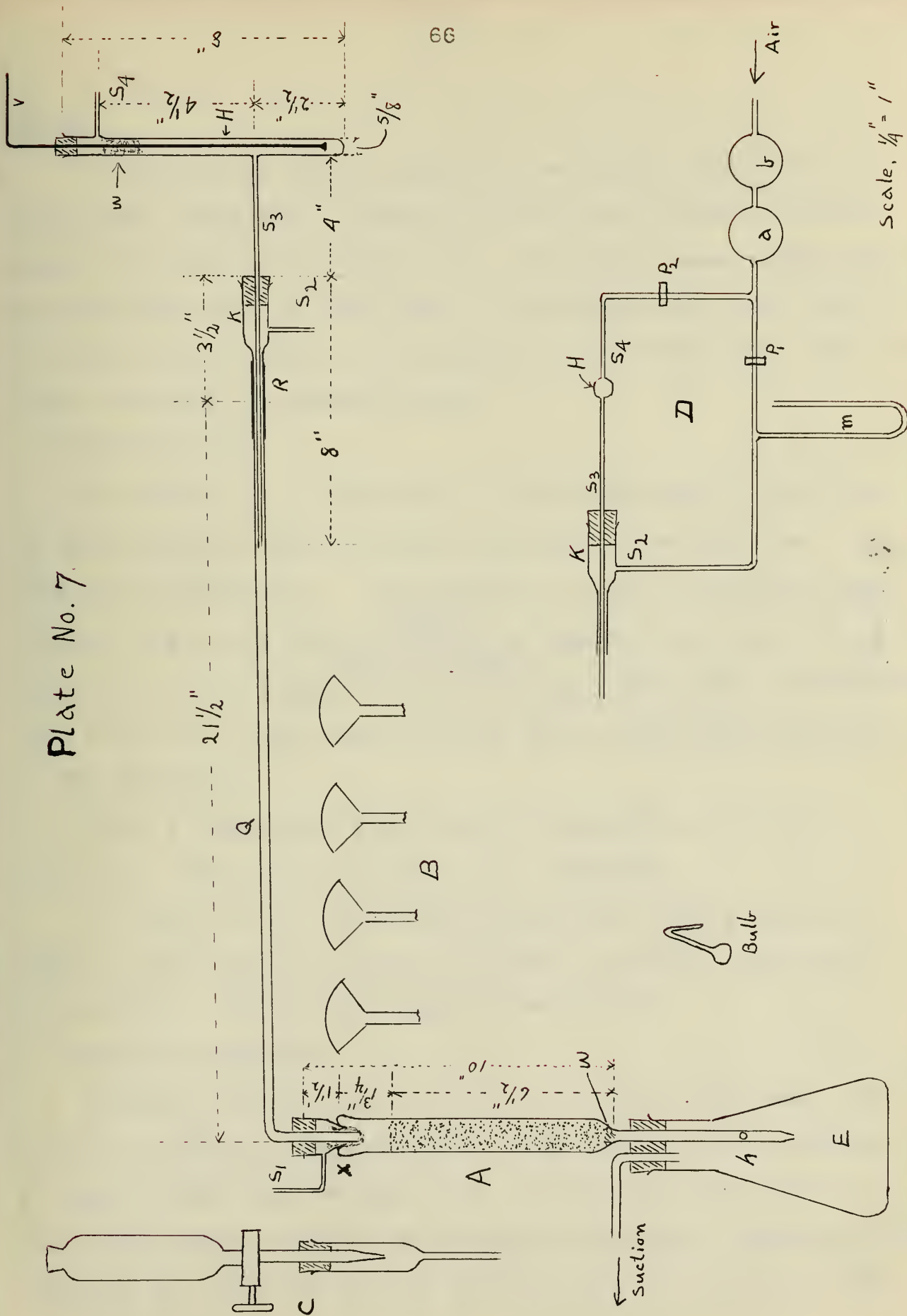
Sample Holder:-

As shown in Plate No. 7, the holder H, now became a simple test tube with two 1 mm. side arms; one S₄, for the entrance of the air, and the other S₃, for the exit of the mixture of air and volatilized sample, the latter leading the mixture far beyond the rubber stopper in the glass adapter, K, which is held against the quartz tube by the rubber tubing, R.

The glass rod, V, is carefully worked downward to break the small glass bulb, which would rest on the bottom of the holder. The bulb shown is somewhat exaggerated in size as compared to the

Plate No. 7.

66



holder.

To protect the rubber stopper of the holder from attack by the organic substance, a tightly fitting plug of glass wool was placed just below the side arm, S_4 . To avoid breakage when heating the holder with a free flame, to volatilize the minute quantity of sample usually held in the capillary neck of the small tube, the holder was made out of Pyrex glass.

Combustion Tube:

As shown by Q, in Plate No. 7, the quartz tube of $1/4$ " bore is held slightly inclined toward and extends down into the absorption apparatus, A. Any bromine or iodine condensing near the exit end of the tube can easily be washed over into A, by removing the rubber stopper in K, and forcing water from a wash bottle into Q from that end, slight suction with a pump being maintained at the same time.

While a transparent quartz tube is desirable, it is not necessary. The writer has used both varieties.

An iron rod, for supporting the inverted V-shaped strip of asbestos board about an inch or so above the quartz tube should be provided. This is not shown in the drawing.

Absorption Apparatus:

Turning to Plate No. 7, it will be seen that this takes the form of a piece of glass tubing 10" long and 1" outside diameter. At about $1-1/3$ " from the upper end, the tube is constricted in a heart-shape manner so that the absorption solution, entering by the side arm, S_1 , must run down the side and drip off the end of the

combustion tube. Glass wool packed around the combustion tube, and also wrapped thinly over the end of the tube prevents any of the products of combustion and decomposition from coming into contact with the rubber stopper.

The lower six to seven inches of the absorption apparatus, A, is filled with common silica, sea sand, which has been previously digested with alkali and acid, and washed. At w there is a thin layer of glass wool.

The extension, leading into the Erlenmeyer flask, E, has a small hole, h, about an inch from the end. This permits the liquid to drop off the end of the tube, without splashing, the residual gases, not absorbed, passing out the hole in the side of the tube. The Erlenmeyer has a volume of 500 cc. and should be strong enough to withstand a slightly reduced pressure.

A small dropping funnel of about 50 cc. capacity is supported so that the adapter, shown in C, can be readily connected to the side arm S₁, by a short length of rubber tubing. The drops falling off the stem of the dropping funnel, constricted at the end to about 2 mm., affords one an opportunity of knowing the rate at which the solution is being introduced into the absorption apparatus.

A guard bottle containing water, to serve as a bubble counter, with an entrance tube of 1/8" bore is placed between the absorption tube and the suction apparatus.

Reagents:

The absorbing and reducing reagents remain the same. The

only exception being that the 25 cc. of 5 N NaOH and 10 cc. of 2 N Na_2SO_3 , together with about 15-20 cc. of water are mixed in the dropping funnel.

General Directions For Operating:

Set up the apparatus as shown in Plate No. 7.

Having placed reagents in the dropping funnel, put the latter in place and connect the end of adapter with the side arm S_1 , by means of a short piece of gum rubber tubing.

An asbestos shield should be used to protect A and the rubber stopper from the heat of the burners.

Place the inverted V-shape piece of asbestos board in place; then light and adjust burners. Next start the water pump, and also the solution to dropping from C. The sand in A should be wetted with the reagents before the products of combustion reach it.

A sample of about 0.2500 grams weighed out and sealed in the small bulb is placed in the lower end of the holder, and the latter connected as shown in the drawing.

A washing bottle, containing concentrated H_2SO_4 and a soda-lime tower, are represented by b and a, respectively. The tower, can be eliminated when there is no halogen in the atmosphere of the room. In that case, the concentrated H_2SO_4 could be replaced by water.

Pinch cocks are indicated by P_1 and P_2 .

The connections between, m, S_2 , a, b and S_4 , as shown in the top view (lower left hand corner), were made with small rubber tubing.

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Adjust the suction so that bubbles pass the counter at the rate of 200 per minute and the solution in the dropping funnel is also running at the rate of 20 to 30 drops (off a 2 mm. funnel) per minute, which will keep sand well soaked with fresh reagent.

If toward the end it appears that not enough solution is present to last out the run, some water may be added, since the reagents are strong enough to stand a dilution with one to two parts of water.

Now close tightly the pinch cock P_2 , but leave P_1 wide open, and break the bulb holding the sample. If, after a couple of minutes, no fog appears in the vacant space above the sand, the pinch cock, P_2 , may be opened slightly. This is to prevent an excessive quantity of the volatile sample being carried over into the combustion tube.

By closing either P_1 or P_2 the change in level of the liquid in the manometer will give an approximate idea of the relative volumes of air flowing through each tube.

The manometer should always show a negative pressure within the apparatus. The writer usually operated with a difference of level varying between two to six inches.

With a substance like ethyl bromide, boiling at 38.4°C , no warming of the holder will be necessary, until toward the close of the run; when a free flame is gradually applied to volatilize the small quantity usually held within the capillary neck of the small bulb, in which the sample was weighed.

Less volatile substances require gentle warming of the holder

usually to within 10-30 degrees of their boiling points.

The rate of combustion, having been regulated so that a gentle but steady fog continues to form in the vacant space above the sand, very little attention is necessary until toward the close of the combustion.

Sometimes a small blue flame will appear at the end of the capillary side arm, S_3 . It is then usually advisable to close down P_2 and open up P_1 and in addition, if the holder is being warmed, to turn down the burner or withdraw the source of heat entirely. When the writer was first experimenting with the above style of apparatus, he used a much shorter capillary side arm, S_3 . On one occasion the material flashed back and the holder was broken, but the substitution of a holder with a longer side arm prevent further explosions. All of the determinations in the following tables were made with a 12" side arm holder.

When the sample is completely volatilized, no further fog will appear. A free flame is then applied to the holder until it has been heated above the boiling point of the substance being analyzed; the burners are then turned out; the inverted V-shaped piece of asbestos removed, as well as all asbestos shields; and the apparatus allowed to cool, the suction still being maintained.

Within less than ten minutes the combustion tube can be rinsed into the absorption apparatus by removing the rubber stopper in the adapter K, and blowing in a stream of water from a wash bottle. Disconnect the absorption train and wash off the end of the combustion tube, outside and inside.

If any reagent is left in the dropping funnel, it is allowed to run rapidly into the absorption apparatus through the glass wool which has been left in the apparatus. The glass wool, including the latter, is now washed with a few small portions of hot water, the sand being sucked nearly dry after each addition of wash water.

The volume of liquid in E will now be about 175 cc. Cool, if warm, and then add 25 cc. of dilute sulphuric acid (1:3 of water). The excess of sulphur dioxide is now oxidized by potassium permanganate solution, and the halogen then determined by the Volhard method.

In the case of compounds with iodine, some of the latter will collect in the end of the combustion tube, but this does not do any harm, when the tube is washed out and then the remaining reagent in the dropping funnel run into A, the crystals of iodine will be readily dissolved and then carried into E with the subsequent washings.

Analyses Of Several Volatile Substances:

By the Combustion Method--

The analyses of twelve volatile substances, using the apparatus shown in Plate No. 7, are to be found in Tables IX to XX inclusive. No data upon the volume of air used is given since it was not collected; the sample was aspirated by the use of a water pump. Under Time, is given the number of minutes required from the breaking of the small bulb, containing the sample, to the end of the combustion, including the washing out of the combustion tube, the absorption apparatus, and the testing for complete washing of the latter and also the water in the gas washing bottle, between E and the water

pump, to see whether by chance any of the halogen had not been absorbed in A. In a few cases no time was recorded.

The values obtained should speak for the efficiency of the method and apparatus developed.

By the Carius Method:-

With two exceptions the comparative analyses by the Carius method are recorded in the same table in which the values by combustion are to be found. In these two cases, one is referred to previous tables.

TABLE IX

Analyses Of Ethylbromide
 C_2H_5Br .

Impure

B.P. of pure = $38.4^\circ C$

Theory = 73.33% Br

Apparatus = Plate No. 7

By Combustion				By Carius		
Det.	Sample (gms.)	Time (min.)	% Br Found	Det.	Sample	% Br Found
114	0.3106	70	72.35	119	0.2479	72.24
115	0.3200	85	72.36	120	0.2244	72.07
116	0.2783	30	72.52	121	0.3027	71.67
117	0.3011	30	72.31	122	0.3225	72.34
118	0.2747	25	72.49	123	0.3370	71.78

TABLE X

Analyses Of Chlorobenzene
 C_6H_5Cl

Pure

B.P. of pure = $132^\circ C$

Theory = 31.52% Cl

Apparatus = Plate No. 7

By Combustion				By Carius		
			% Cl Found			% Cl Found
124	0.3350	90	31.28	130	0.2304	31.17
125	0.2720	90	31.65	131	0.1982	31.26
126	0.2579	115	31.76	132	0.2721	31.75
127	0.2821	70	31.47			
128	0.3034	95	31.70			
129	0.3399	80	31.79			

STATE OF NEW YORK
IN SENATE
January 1, 1891.

REPORT OF THE
COMMISSIONERS OF THE LAND OFFICE

LANDS BELONGING TO THE STATE			LANDS BELONGING TO THE PEOPLE			TOTAL
ACRES	SQUARE MILES	VALUE	ACRES	SQUARE MILES	VALUE	
1,000,000	15.625	\$1,000,000	1,000,000	15.625	\$1,000,000	\$2,000,000
1,000,000	15.625	\$1,000,000	1,000,000	15.625	\$1,000,000	\$2,000,000
1,000,000	15.625	\$1,000,000	1,000,000	15.625	\$1,000,000	\$2,000,000
1,000,000	15.625	\$1,000,000	1,000,000	15.625	\$1,000,000	\$2,000,000
1,000,000	15.625	\$1,000,000	1,000,000	15.625	\$1,000,000	\$2,000,000

OF THE
LANDS BELONGING TO THE
STATE OF NEW YORK

REPORT OF THE
COMMISSIONERS OF THE LAND OFFICE

LANDS BELONGING TO THE STATE			LANDS BELONGING TO THE PEOPLE			TOTAL
ACRES	SQUARE MILES	VALUE	ACRES	SQUARE MILES	VALUE	
1,000,000	15.625	\$1,000,000	1,000,000	15.625	\$1,000,000	\$2,000,000
1,000,000	15.625	\$1,000,000	1,000,000	15.625	\$1,000,000	\$2,000,000
1,000,000	15.625	\$1,000,000	1,000,000	15.625	\$1,000,000	\$2,000,000
1,000,000	15.625	\$1,000,000	1,000,000	15.625	\$1,000,000	\$2,000,000
1,000,000	15.625	\$1,000,000	1,000,000	15.625	\$1,000,000	\$2,000,000

TABLE XI

Analyses Of Ethyl Iodide
 C_2H_5I

Impure

B.P. of pure = $72.2^\circ C$

Theory = 81.34% I

Apparatus = Plate No. 7

By Combustion

By Carius

Det.	Sample (gms.)	Time (min.)	% I found	Det.	Sample (gms.)	% I Found
133	0.4522	67	81.47	135	0.3028	81.47
134	0.4074	98	81.48	136	0.4750	80.90
				137	0.2708	81.20

TABLE XII

Analyses Of Brombenzene
 C_6H_5Br

Pure

B.P. of pure = $157^\circ C$

Theory = 50.90% Br

Apparatus = Plate No. 7

By Combustion

By Carius

Det.	Sample	Time	% Br found	Det.	Sample	% Br Found
138	0.2520	--	51.01	141	0.3826	51.23
139	0.3147	--	50.93	142	0.3632	51.26
140	0.2802	120	50.83			

TABLE XIII

Analyses of Allyl Bromide¹
 C_3H_5Br

Impure

B.P. of pure = 76° C

Theory = 64.57% Br

Apparatus = Plate No. 7

By Combustion

By Carius

Det.	Sample	Time	% Br Found	Det.	Sample	% Br Found
143	0.2345	120	62.87	146	0.2141	61.02
144	0.2431	110	62.56	147	0.2252	61.70
145	0.2342	120	63.61	148	0.2842	62.12

¹ Difficult sample to get into small
 bulb without decomposition

TABLE XIV

Analyses of Ethylene Chloride
 $C_2H_4Cl_2$

Pure

B. P. of pure = 83° C

Theory = 71.71% Cl

Apparatus = Plate No. 7

By Combustion

By Carius

Det.	Sample	Time	% Cl Found	Det.	Sample	% Cl Found
149	0.2688	90	71.66	152	0.2773	71.68
150	0.2868	120	71.68	153	0.2414	72.04
151	0.2521	120	71.82			

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THE CLERKS OF THE TREASURY OF THE UNITED STATES
OF THE DEPARTMENT OF THE TREASURY
OF THE UNITED STATES OF AMERICA

NAME	AGE	DATE OF BIRTH	DATE OF DEATH	DATE OF BURIAL	DATE OF CREMATION	DATE OF INTERMENT
John Doe	35	1850	1885	1885	1885	1885
Jane Doe	32	1852	1885	1885	1885	1885
John Doe	30	1854	1885	1885	1885	1885
Jane Doe	28	1856	1885	1885	1885	1885

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NAME	AGE	DATE OF BIRTH	DATE OF DEATH	DATE OF BURIAL	DATE OF CREMATION	DATE OF INTERMENT
John Doe	35	1850	1885	1885	1885	1885
Jane Doe	32	1852	1885	1885	1885	1885
John Doe	30	1854	1885	1885	1885	1885
Jane Doe	28	1856	1885	1885	1885	1885

TABLE XV

Analyses Of Butyl Bromide
 C_4H_9Br

Impure

B.P. of pure = 100° C

Theory = 58.34% Br

Apparatus = Plate No.7

By Combustion

By Carius

Det.	Sample	Time	% Br Found	Det.	Sample	% Br Found
154	0.6136	128	58.16	157	0.2429	58.71
155	0.3231	58	58.14	158	0.2937	58.50
156	0.4751	123	58.11			

TABLE XVI

Analyses Of Benzal Chloride
 $C_6H_5CHCl_2$

B.P. of pure = 212° C

Theory = 44.05% Cl

Apparatus = Plate No. 7

Det.	Sample	Time	% Cl Found	Det.	Sample	% Cl Found
159	0.2965	90	44.51	163	0.2588	44.82
160	0.2332	90	44.41	164	0.2676	44.28
161	0.3049	75	44.47			
162	0.2129	--	44.56			

TABLE XVII

Analyses of Carbon Tetrachloride
 CCl_4

Pure

B. P. of pure = 78°C

Theory = 92.20% Cl

Apparatus = Plate No. 7
By Carius

By Combustion

Det.	Sample	Time	% Cl Found
------	--------	------	------------

Det.	Sample	% Cl Found
------	--------	------------

165	0.2494	106	91.92
-----	--------	-----	-------

See Determinations 109-113 Table VIII		
--	--	--

166	0.2614	93	91.37
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TABLE XVIII

Analyses Of Chloroform, CHCl_3

Sample C

Impure

B. P. of pure = 61°C

Theory = 89.02% Cl

Apparatus = Plate No. 7

By Combustion

By Carius

Det.	Sample	Time	% Cl Found
------	--------	------	------------

Det.	Sample	% Cl Found
------	--------	------------

167	0.2747	90	88.83
-----	--------	----	-------

See Determinations 91-100 Table VI		
---------------------------------------	--	--

168	0.2840	85	88.64
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TABLE XIX

Analyses Of Ethylene Bromide
 $C_2H_4Br_2$

Impure

B.P. of pure = 129° C

Theory = 85.09% Br

Apparatus = Plate No. 7

By Combustion

By Carius

Det.	Sample	Time	% Br Found	Det.	Sample	% Br Found
169	0.3934	180	84.51	173	0.2800	84.45
170	0.2013	145	84.45	174	0.2955	84.59
171	0.2114	95	84.27			
172	0.2178	105	84.41			

TABLE XX

Analyses Of Chlorpicrin¹
 CCl_3NO_2

Impure (?)

B.P. of pure = 113° C

Theory = 64.72%

Apparatus = Plate No. 7

Det.	Sample	Time	% Cl Found	% CCl_3NO_2	Det.	Sample	% Cl	% CCl_3NO_2
175	0.3046	155	64.55	99.74	179	0.3443	64.14	94.88
176	0.1819	95	64.77	100.08	180	0.2448	64.47	99.62
177	0.2057	63	64.47	99.62	181	0.2946	64.53	99.70
178	0.2235	68	64.50	99.66	182	0.2342	64.60	99.81

¹ Material prepared by R. W. Hale, Jr., Johns Hopkins University

PART IV

Analysis Of Substances With More Than One Halogen
Present

W. M. Dehn has shown that any two halogens in a binary mixture of halides may be calculated from the data obtained by the determination of the silver equivalent by means of the Volhard method and from the weight of the mixed silver halides formed during this determination.²⁵ It was believed that the necessary data for the determination of any two halogens in any organic compound might be obtained by the combustion of the sample and absorption and estimation of the evolved halogen as described in the analysis of compounds contained one halogen.

Mr. G. H. Coleman, who is engaged at the University of Illinois in a study of the reactions of nitrogen trichloride, kindly supplied the writer with a quantity of a product from the reaction between nitrogen trichloride and ethyl bromide, believed to be ethylene chlor-bromide, C_2H_4ClBr .

His method of analysis was to obtain the weight of the combined mixed halides by the Carius method and the weight of the silver in the precipitate by reducing the mixed halides in the crucible (a gold Munroe crucible was used) with hydrazine sulphate in the presence of sodium hydroxide,²⁶ the silver left in the crucible being washed, dried and weighed.

The values he obtained were as follows:

% Bromine found	% Chlorine found
38.9	21.6

39.4 21.5

39.2 21.5

The values obtained by the writer, using the above proposed method are:

Det.	Wt. of Ag Halides	% Bromine found	% Chlorine found
183	0.3778	41.51	20.33
184	0.3955	41.30	20.53

These are corrected for the blank obtained with the reagent used. An error may have been thus introduced, for the blank amounted to 1.18 cc. of 0.10058 N AgNO_3 solution, or expressed in grams of AgCl , 0.0172 grams. There is the possibility that the blank is not entirely due to the presence of chlorides.

The theoretical values are:

% Bromine = 55.73

% Chlorine = 24.74

Apparently the material analyzed was either not chlorbromethane, or else some foreign material was present, with a boiling point about the same, between 79° and 80° C. The closeness of the values obtained by the two different methods of analysis warranted further trials of this scheme.

Accordingly, a known substance, a sample of Kahlbaum's dichlorbrommethane, CHCl_2Br , was next analyzed. The data obtained is recorded in Table XXI.

The values for chlorine and bromine were not at all satisfactory. A perusal of the data given indicates that the trouble lies in the weights of the precipitates of the silver halides.

The following are the names of the persons who have been elected to the office of

Ward	Name	Address	Age
1st	John A. Smith	123 Main St.	35
2nd	James B. Jones	456 Elm St.	42
3rd	William C. Brown	789 Oak St.	28
4th	Robert D. White	101 Pine St.	55

The following are the names of the persons who have been elected to the office of

Ward	Name	Address	Age
5th	Charles E. Green	234 Maple St.	30
6th	Thomas F. Black	567 Cedar St.	48
7th	Henry G. Gray	890 Birch St.	25
8th	George H. Hall	112 Spruce St.	60

The following are the names of the persons who have been elected to the office of

Ward	Name	Address	Age
9th	Edward I. King	345 Walnut St.	38
10th	Frank J. Lee	678 Hickory St.	45
11th	Samuel K. Scott	901 Ash St.	22
12th	David L. Adams	1234 Chestnut St.	58

The following are the names of the persons who have been elected to the office of

Ward	Name	Address	Age
13th	John M. Baker	4567 Broadway	32
14th	William N. Carter	7890 Madison Ave.	40
15th	Robert O. Evans	1011 Park St.	27
16th	Thomas P. Foster	1234 Union St.	52

The following are the names of the persons who have been elected to the office of

Ward	Name	Address	Age
17th	Charles Q. Gibson	2345 Broadway	35
18th	James R. Harris	5678 Madison Ave.	43
19th	William S. Jones	8901 Park St.	29
20th	Robert T. King	1234 Union St.	57

The following are the names of the persons who have been elected to the office of

Ward	Name	Address	Age
21st	George U. Lewis	3456 Broadway	37
22nd	Henry V. Martin	6789 Madison Ave.	46
23rd	Samuel W. Nelson	9012 Park St.	24
24th	David X. Olsen	1234 Union St.	59

They not only vary, but in every instance are too high, providing one assumes that the weight of combined halide, reduced to the basis of a 0.2000 gram sample of CHCl_2Br , obtained by the Carius method, is correct; and there is no reason in the writer's mind for not doing so. The titration data is very consistent and values obtained in previous mono-halogen compounds warrant the belief that it is correct.

On investigation as to the cause of the increment in the weights of the precipitates, it was found that the absorption solution, after passing thru the sand, gave up a gelatinous precipitate of silica on acidifying and allowing to stand for a short time. To make certain that the reagents themselves were not contributing the silica, solutions of sodium hydroxide and sulphite were prepared which were known to be free from such, yet, while the quantity of silica was slightly smaller, it was still appreciable and large enough to produce the error obtained.

The question arises as to the actual error that would be produced by either an error of 0.10 cc. in the titration, or 0.0010 gram in the weight of the precipitate of the silver halides. The former, if plus, will increase the chlorine value by 0.7 plus percent, and lower that for bromine 1.2 plus percent; the latter, if plus, lowers the chlorine value 0.4 plus percent and increases that for bromine 0.9 plus percent.¹ It thus becomes evident that the analytical work must be carried out very accurately, otherwise,

¹ This is based upon the values that should be obtained in a 0.2000 gram sample of pure dichlorobromomethane and using a solution of silver nitrate of the same strength as above.

the values obtained will be incorrect. Of course, this applies to most indirect analyses of this type.

The writer feels that a satisfactory solution of the difficulty can be worked out and he regrets that time was not available to carry this special investigation further.

TABLE XXI

Analyses of Dichlorobrommethane, CHCl_2Br B. P. of pure = 91°C Theory (= 43.29% Chlorine
(= 48.78% Bromine)

Det.	Sample gms.	Time min.	Wt. of Ppt.		Titration cc. 0.10058N		% Cl	% Br
			Actual	Per 0.2000 gram	Actual	Per 0.200 gram		
183	0.2891	95	0.8278	0.5727	51.35	35.53	40.14	54.38
184	0.3215	95	0.9360	0.5823	57.20	35.58	35.83	62.25
185	0.3213	80	0.9303	0.5791	57.13	35.56	36.93	59.68
186	0.3237	93	0.9319	0.5758	57.52	35.54	39.24	58.06
187	0.2821	73	0.8141	0.5622	50.22	35.60	38.03	57.40
			Average = 0.5744		Average = 35.56			

Some additional data on dichlorobrommethane:

1. Titration, per 0.2000 gram, if pure (calculated) 36.41 cc.
2. Wt. of ppt. per 0.2000 gram, if pure (calculated) 0.5792 gm.
3. Wt. of ppt. obtained from Carius (Av. of 2 dets.) 0.5745 gm.
4. Percentage purity, based solely on above titration 97.66%
5. Percentage purity, based solely on above weight of
precipitate, obtained from Carius 96.93%
6. Percentage of halogens, based on av. titration and
av. weight of precipitate (Carius) 38.76% Cl
55.58% Br

PART V

Analysis of Difficultly Volatile and Solid Substances

Preliminary:-

While this is a phase which does not properly come under the title of this thesis, yet the results obtained with easily volatile substances suggested that the scheme could be applied to more difficultly, or even non-volatile substances.

A sample of material whose analyses are recorded in Table XXII was furnished the writer; it being taken since an analysis by the Carius method had already been made by the person preparing the substance.

The apparatus used was that shown in Plate No. 7. The first analyses are Nos 188-191, inclusive, which were not very satisfactory.

The trouble lay in the fact that the substance eventually charred when the holder was heated and tarry material condensed in the side arm leading into the combustion tube and it was impossible to volatilize this without burning the rubber connection and the stopper.

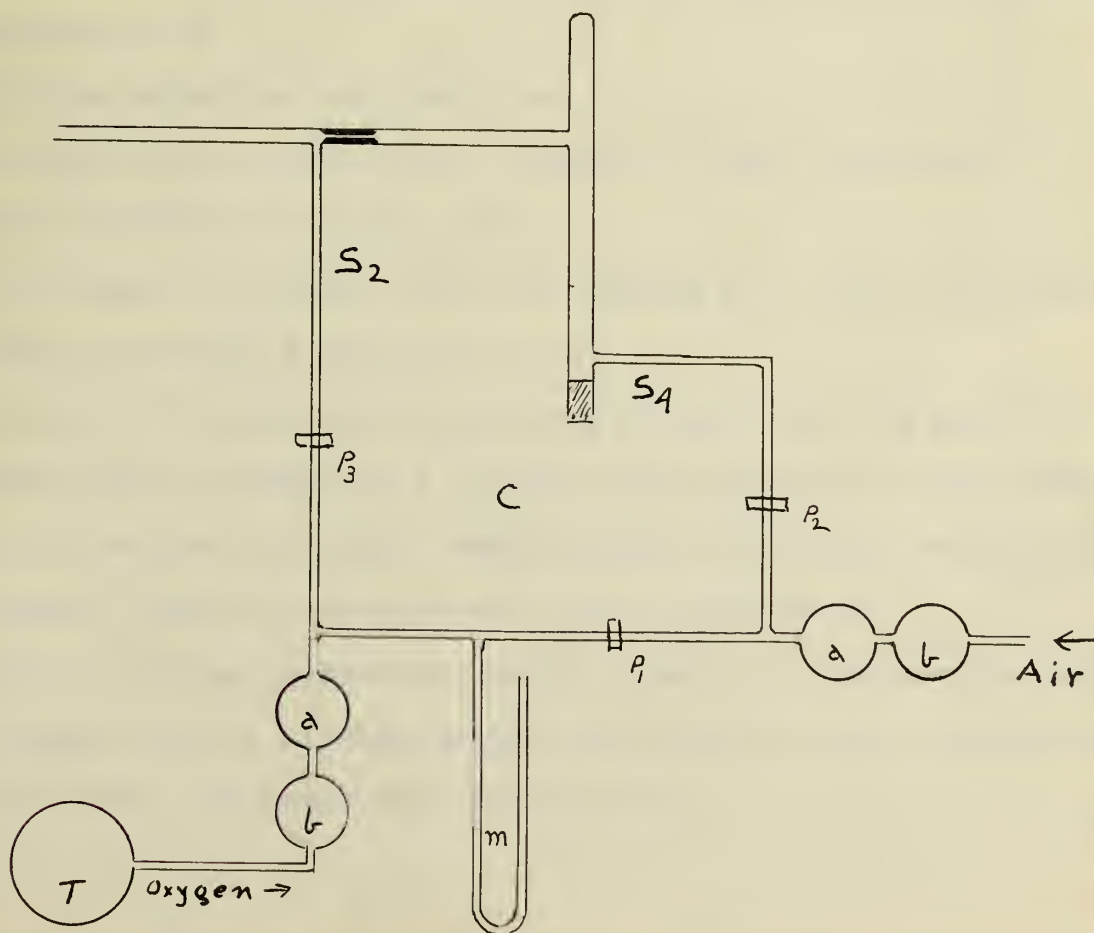
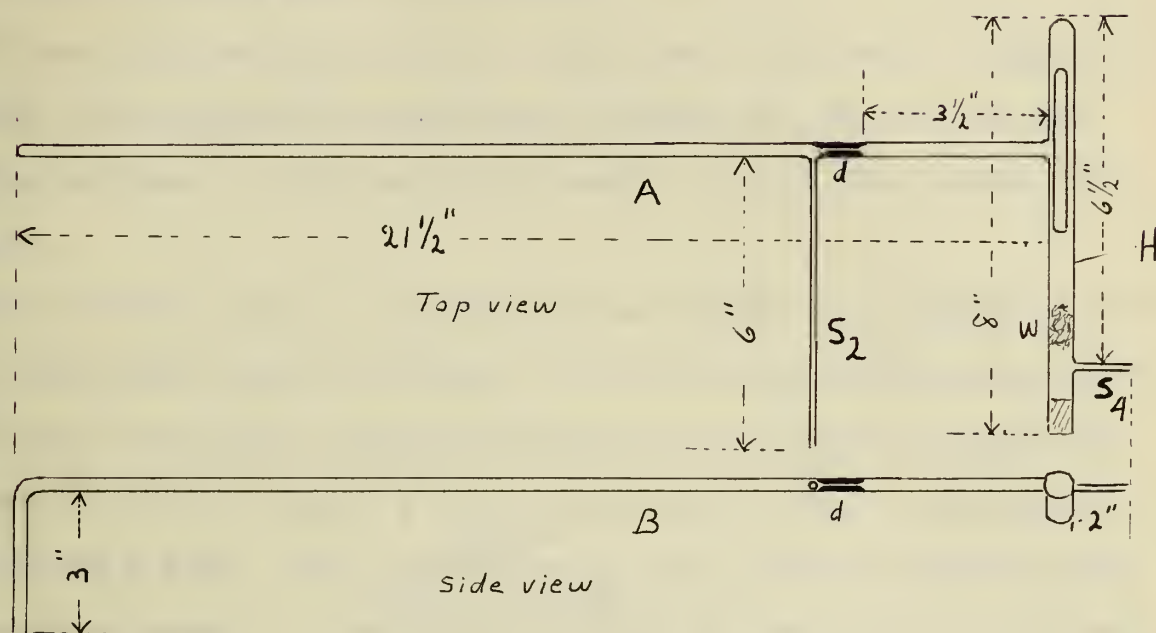
The values obtained, although they did not check very well, indicated that the scheme would work satisfactorily, providing an apparatus was designed which permitted the burning of the condensed tarry material just mentioned.

Determination Of Halogen:-

Sample Holder and Combustion Tube:

The modification worked out is shown in Plate No. 8. The

Plate No. 8.

Scale, $\frac{1}{4} = 1''$ 

dimensions are given in A and B to scale. The holder and combustion tube consist of one piece of transparent quartz tubing; also the 2 mm. side arms, S_2 and S_4 .

A top view is shown in A; a side view in B; and a diagrammatic drawing, indicating the connections between S_4 , S_2 , m, the gas washing bottles, b, the soda-lime towers, a, and the oxygen tank, T, in D.

The holder proper, H (made from an eighth-inch length of 5/8" bore transparent quartz tubing), is not in a vertical position in this case, but rather inclined downward at an angle of about 20° to the horizontal, when all is in position to make a combustion. This allows a boat, with sample, to be slid and not dropped into the position shown. The sample on melting then runs to the lower or sealed end of H.

Absorption Apparatus and Reagents:

The absorption apparatus and reagents remain unchanged.

General Directions for Operating:

In the case of solids, they are weighed out into a porcelain boat, which is shown in position in A.

A liquid like that used in determinations Nos. 196 and 197 (See Table XXIII), which has a slight vapor pressure at room temperature, is weighed in a small sealed bulb, the latter being broken in the manner used in the apparatus shown in Plate No. 7.

Liquids with no appreciable vapor pressure at room temperature can be weighed out in a small quartz tube, open at one end, and then slid down toward the lower end of the holder.

The operation during combustion is much the same as in the case of the apparatus shown in Plate No. 7, except that the aspiration should now be run only about two-thirds as rapidly during the actual combustion, since with the introduction of pure oxygen just beyond the constriction in the combustion tube, less residual gases are passing through the absorption apparatus.

In general, the pinch cock, P_1 , remains closed during the combustion, only air passing via P_2 , and pure oxygen via P_3 .

In all cases one should use about two or three times as much oxygen as air, the latter being at the rate of about 100 small bubbles per minute.

One should see that the fog appearing in the space above the sand in the absorption apparatus forms continuously, but does not become dense. This will depend largely upon the rate of aspiration, but also upon the rate of introduction of pure oxygen. If the latter is slow and the former excessive, the air will be drawn too rapidly via P_2 , which may result in too much of the volatilized sample being carried into the combustion tube and charring may result. It will be found, however, that it is very easy to regulate the rate of aspiration and the flow of air and oxygen so that the sample will be volatilized and burned smoothly.

These difficultly non-volatile substances will need the application of heat to the holder; the proper position of the initially small and steady flame is directly under the point, midway between the plug of glass wool, w , and the near end of the combustion tube. Should fog not appear shortly in the absorption apparatus, the flame may be increased. If that does not suffice, the

holder between the flame and the sealed end may be covered with an inverted V-shape piece of asbestos board. If the material still does not begin to volatilize, then the flame may be gradually moved toward it.

Care must be taken that the material does not char too rapidly and thus set free more combustible gases than can be completely burned by the oxygen entering the side arm S_2 . It will be found that this can be easily managed, and having made the proper regulations, the combustion will go on without much attention.

Toward the close, it will be found that the lower end of H, will be coated with carbon. After heating the end carefully for a few minutes with only air passing thru H, the pinch cock, P_1 , is opened, and P_2 closed. The deposit of carbon will burn up readily as soon as the pure oxygen reaches it, providing of course that H is being heated to a dull red. The same applies to the deposit in the 1/4" bore tube between H and d, in the combustion tube. Occasionally a small deposit may be found in the side arm S_2 , which, of course, should also be burned out.

When all is burned out, close the valve on the oxygen tank and see that P_1 and P_2 are open. Now turn out the four burners, take away the pieces of asbestos board and remove the rubber tubing from the ends of S_2 and S_4 . When the apparatus is almost at room temperature, remove the rubber stopper, glass wool, and boat or whatever the sample was weighed in, and then, with water pump still going, twice as rapidly as during the combustion, flood H with water from a wash bottle, rinsing any products remaining into the

absorption train.

(The writer then steamed out the whole apparatus by inserting the rubber stopper in H and heating the water remaining in it to boiling.)

When the small quantity of water in it has been evaporated, the combustion tube is heated for a moment to remove the water condensed therein and then the apparatus is allowed to cool.

From here on the procedure is the same as in the case of the apparatus in Plate No. 7.

Analysis Of Several Substances:

The values obtained upon the substances analysed, using this modified apparatus are given in Tables XXII and XXIII.

No Carius determinations were made upon the substances given under Nos. 198-205, partly because the material being used was thought to be very pure, and partly because of lack of time.

While only a few determinations have been made upon this class of substance, yet it appears that the method is satisfactory, when an apparatus like the one shown is used.

To ascertain whether this style of apparatus would give as good results on rather volatile substances, as that shown in Plate No. 7, two analyses were made upon this same ethylene chloride used in determinations 149-153, inclusive. The following was obtained:

Determination	Sample	% Chlorine
206	0.2181	71.62
207	0.1971	71.58

TABLE XXII

Analyses of p-Brom-o-(β , γ -dibromopropyl)Phenyl
Benzoate

O=C(Oc1ccc(Br)cc1)C2CC(Br)CC2Br

Fairly pure

M. P. =

Theory = 50.29% Br

Apparatus used¹

By Combustion				By Carius		
Det.	Sample	Time	% Br Found	Det.	Sample	% Br found
188	0.3066	75	48.97	2	0.2192	50.33
189	0.4815	140	48.63	194	0.2442	50.10
190	0.2439	125	49.01	195	0.2955	50.02
191	0.2427	90	49.35			
192	0.2441	95	50.09			
193	0.2451	60	49.98			

¹ For Nos. 188 to 191, inclusive, see Plate No. 7, and for Nos. 192 and 193, see Plate No. 8, for style of holder and combustion tube. Absorption apparatus remains the same as in Plate No. 7.

² Data for this analysis furnished by Mr. V. L. Harnack, who also supplied the sample of p-Brom-o-(β , γ -dibromopropyl)Phenyl Benzoate). His problem was the Synthesis of Cyclic Ethers. He had dried the Gooch with precipitate for only one hour at 110° C and had only run one analysis. The writer dried his Gooches without and with precipitates to constant weight at 130° C.

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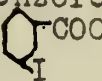
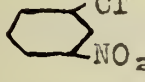

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TABLE XXIII

Analyses Of Several Difficultly Volatile Substances

Using Tank Oxygen			Apparatus ¹			
Det.	Substance and formula	M.P. or B.P	Sample Time (gms.) (min.)	% Halogen by Theory	% Halogen found	
196	P-Bromophenyl β -Bromallylether  <chem>BrC1=CC=C(C=C1)OCH2CBr=CH2</chem>	Boils at 171°C at 22 mm.	0.3194 130	54.76	54.06	
197	Ditto	Ditto	0.2998 165		54.51	
198	Hexachlorbenzene, <chem>C6Cl6</chem>	M.P.=229°C B.P.=326°C	0.2431 80	74.73	74.60	
199	Ditto	Ditto	0.2484 75		75.01	
200	M-Iodobenzoic acid  <chem>O=C(O)c1ccccc1I</chem>		0.3776 100	50.98	51.09	
201	Ditto		0.3706 105		50.98	
203	M-Chlornitrobenzene  <chem>Clc1cccc(c1)[N+](=O)[O-]</chem>	M.P.=44.4°C B.P.=235.6°C	0.2800 75	22.51	22.70	
204	Ditto	Ditto	0.3167 70		22.52	
205	P-Bromaniline  <chem>Nc1ccc(Br)cc1</chem>	M.P.=66.4°C B.P.=decomp.	0.3198 95	46.18	46.47	

¹ For holder and combustion tube see Plate No. 8, for absorption apparatus see Plate No. 7.

The material used in determinations 196 and 197 was kindly furnished by Mr. S. G. Powell whose problem was Unsaturated Phenyl Ethers And Their Rearrangements. By Carius he found 54.1 and 54.4% bromine.

The substances used in determinations 198 to 205, inclusive, were Kahlbaum's. Time was not available for checking up the analyses by Carius.

S U M M A R Y

1. A simple, rapid and accurate method for the quantitative determination of chlorine, bromine and iodine in volatile organic substances has been developed. The material, volatilized with air, is drawn thru a heated quartz tube, the product absorbed in alkaline sodium sulphite solution and titrated. No catalytic agent is used.

2. With a slight modification of the apparatus, the method, with the partial use of pure oxygen, is applicable to non-volatile and solid substances, with equally satisfactory results.

3. An electrically heated, multiple, and continuous bomb furnace has been developed.

4. An electrically illuminated titration table has been designed.

VII

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VIII

Biography

The author of this thesis was born in Geneseo, Illinois, on December 27, 1883.

He received his grade school and high school education in Detroit, Michigan, where he was graduated from the Western High School in 1906.

His undergraduate preparation was received at the University Michigan, where he received the degree of Bachelor of Science in 1911. During his last two years at Michigan, he held a student assistantship in chemistry.

From 1908-1909, also during the summer of 1911, he held the position of assistant chemist, with the Detroit Chemical Works, Detroit, Michigan.

From 1911 to 1915, including the summer sessions of 1913, 1914 and 1915, he was an instructor in general chemistry and qualitative analysis at the Case School of Applied Science.

From 1915 up to date, including the summer session of 1918, he has been an assistant in chemistry at the University of Illinois.

In 1917 he received the degree of Master of Science from the University of Illinois.

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